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ORGANIC

AND

MEDICAL CHEMISTRY.

LEFFMANN.

A

COMPEND

OF

ORGANIC AND MEDICAL CHEMISTRY;

INCLUDING

URINARY ANALYSIS AND THE EXAMI- NATION OF WATER AND FOOD.

BY

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DENTAL SURGERY, AND OF CLINICAL CHEMISTRY AND HYGIENE
IN THE PHILADELPHIA POLYCLINIC.

TO
DR. CHARLES M. CRESSON,
IN WHOSE LABORATORY
I LEARNED THE PRACTICE OF CHEMISTRY,
AND TO WHOM I AM INDEBTED
FOR INNUMERABLE DISINTERESTED KINDNESSES,
THIS WORK IS
RESPECTFULLY INSCRIBED.

PREFACE.

A work like the present can, of course, claim no originality. Here and there, perhaps, the author may contribute a fact or inference from his own experience, but the great bulk of the matter will be drawn from his library. The merits of such books lie only in the accuracy and perspicuity with which the facts of the science are detailed, and in the proper adjustment of the space assigned to different topics. In the following pages I have tried to meet these requirements; how far I have succeeded is for others to judge.

The compactness with which the book is printed Ras enabled a large amount of matter to be inserted; and I have sought to supplement this by using a somewhat condensed style, notably by following the example of Tidy, and expressing the composition and properties of groups of bodies in tabular form. But little space has been given to graphic formulæ.

The work will, I think, be found to contain a sufficient outline of organic and medical chemistry to serve the purpose of the student, especially one pursuing the study of medicine.

The usual care has been taken in the proof-reading, but, no doubt, errors have been overlooked. I am indebted to my assistant—Mr. William Beam—for aid in the preparation of the work. H. L.

S. E. Cor. 13th and Locust Sts.
    April 30th, 1884.

CONTENTS.

COMPEND

OF

ORGANIC AND MEDICAL CHEMISTRY.

NATURE OF ORGANIC BODIES.

Organic Chemistry is primarily the study of the substances which form part of the tissues of plants and animals. Not only are these very numerous, but by various influences, such as action of heat or of oxygen, many new bodies may be formed, and these new bodies are also included in organic chemistry. The great majority of the substances found in living things cannot be produced by artificial means. At the outset we must carefully distinguish between an ORGANIZED and an ORGANIC body. The former has a definite structure, generally cellular, and possesses the specific action known as vitality. Organic bodies, on the other hand, may have any structure, or be structureless. All organized bodies are organic, but all organic bodies are not organized. For the recognition of the organic nature of any substance the action of heat usually suffices. It causes decomposition, with evolution of smoky, strong-smelling vapors; a residue of carbon remains which can be burned off by heating strongly in the air. Sulphuric acid also produces a characteristic blackening, due to liberation of carbon. The presence of nitrogen is usually indicated by a disagreeable odor like that of burning wool. A more delicate test is by heating the body with an alkali, by which ammonia is formed. Organized bodies are in general easily recognized by the microscope.

The elements which enter into the formation of organic bodies are few in number. Carbon, hydrogen, nitrogen and oxygen are by far the most frequent; sulphur, phosphorus and iron are found to a limited extent, principally in the most highly organized tissues of animals. During the last twenty-five years many artificial bodies have been formed, in which elements such as mercury, bismuth, arsenic, chlorine and iodine have been introduced; these, although analogous to the more natural organic bodies, are not capable of forming part of the healthy tissues. Carbon is present in

almost all organic bodies, and for this reason organic chemistry has some-
times been called the " chemistry of the carbon compounds." Hydrogen
is also almost always present; oxygen somewhat less frequently; nitrogen
still less frequently; while sulphur, phosphorus and iron are rather
exceptional in their occurrence. The following table gives a list of bodies
belonging to different classes in organic chemistry, and shows how many
changes may be made in the combinations of these few elements. The
compounds all occur ready formed in nature :—

$C_{10}H_{16}$ ....Oil of turpentine.
$C_{12}H_{22}O_{11}$....................Cane sugar.
$C_{10}H_{14}N_2$.....................Nicotine (from tobacco).
$C_{17}H_{19}NO_3$...................Morphine (from opium).
$C_2H_7NSO_3$....................Taurine (from bile).
$C_3H_9PO_6$ ....Phospho-glyceric acid (from brain).
$C_{32}H_{32}FeN_4O_6$ ....Hæmatine (from blood).

Proximate and Ultimate Composition. The tissues of plants and
animals, or the products of their decomposition, are generally mixtures of
several independent substances. Thus butter is a mixture of four or five
fats; common rosin contains two or sometimes three distinct bodies; opium
and Peruvian bark are still more complicated, and brain and muscle
structures are so complicated that as yet perfect analyses have not been
made of them. The substances which thus exist naturally together in a
state of mixture are called PROXIMATE PRINCIPLES, the separation and
identification of them is called PROXIMATE ANALYSIS, and such of them as
give characteristic qualities to the articles in which they occur are gener-
ally called ACTIVE or ESSENTIAL PRINCIPLES ; atropine, for instance, is the
active principle of belladonna, for although many different bodies are
contained in the belladonna leaf, atropine is the one upon which its physio-
logical activity depends. The ULTIMATE PRINCIPLES of a substance are
the elements (carbon, hydrogen, etc.) which it contains.

Ultimate analysis, that is the determination of the proportions
of the elements that may be present, although requiring care in
manipulation, is practically the same for all organic compounds. It
consists in burning the body in a full supply of oxygen, by which the
carbon is converted into carbon dioxide and the hydrogen into water.
These may be collected and weighed, and the amounts of carbon and
hydrogen corresponding to these weights may be easily determined by calcu-
lation. Oxygen, if present, is generally determined by the difference
between the weight of the original body and the sum of the weights of the
carbon and hydrogen ; nitrogen, chlorine, sulphur, or other less common

elements must be determined by special methods. The following shows the outline of a simple analysis :—

46 grains of alcohol—which contains only C H and O—if burned completely, produces—

$$88 \text{ grs. of } CO_2 \text{ equivalent to } 24 \text{ grs. of C.}$$
$$54 \text{ grs. of } H_2O \quad \text{``} \quad \text{``} \quad 6 \text{ grs. of H.}$$

The sum of the carbon and hydrogen is 30, which subtracted from 46, the weight of the alcohol, gives 16 as the weight of the oxygen.

Proximate analysis is a problem much more complicated ; special processes have to be devised for most of the examinations. The following very simple instance of a proximate analysis will be sufficient to illustrate the principle of the methods used. Suppose an organic mixture is known to contain starch, sugar, rosin and volatile oil; by a gentle heat the volatile oil may be extracted, alcohol will dissolve the rosin, cold water the sugar, and hot water the starch.

Transformation of Organic Bodies. It has been mentioned above that, in addition to the bodies found ready-formed in plants and animals, a large number of derivative substances are known. These are produced by a great variety of methods, some of which are of general application.

(*a*) ACTION OF HEAT. The great majority of organic compounds are changed by heat, some only slightly, others completely. Many are converted into new bodies, which escape in the condition of vapors, and may be subsequently condensed. In this way coal, when heated, gives rise to coal gas, coal tar, pitch, etc., these products being mixtures of many *proximate* principles. Such a process is called destructive distillation.

(*b*) ACTION OF OXYGEN. At high temperatures most organic bodies burn, producing carbon dioxide and water. At low temperatures the oxygen may enter slowly into combination, or, as frequently happens, may substitute the hydrogen, the substitution taking place in the proportion of one atom of oxygen for every two atoms of hydrogen removed. In both these actions the resulting bodies are generally acids.

(*c*) ACTION OF NITRIC ACID. This varies with the temperature and degree of concentration of the acid. When very strong and cold acid is used, the action is generally a substitution of the molecule NO_2 for H, giving rise to a series of bodies called *nitro-compounds*. When the acid is weak or hot, the action is usually the direct addition of oxygen, according to methods given in the preceding paragraph.

(*a*) ACTION OF CHLORINE. Chlorine sometimes enters into direct combination, but usually displaces the hydrogen and takes its place, atom for atom. Bromine and iodine act in the same manner.

The substituting actions of oxygen, nitric acid, chlorine, etc., give rise to a very important series of compounds, which are more completely explained below.

(e) ACTION OF DEHYDRATING AGENTS. These are bodies—sulphuric acid, and phosphoric anhydride, for example—which have a high affinity for water. They act by abstracting hydrogen and oxygen in the proportion of two atoms of H to one of O.

(f) SO–CALLED NATURAL CHANGES. These are *Fermentation*, *Putrefaction* and *Decay*. They are now known to depend on special conditions and not to be truly spontaneous, but the exact nature of them is still a question. Many scientists are of the opinion that minute living organisms are the agents.

FERMENTATION is a process by which certain organic bodies, particularly forms of sugar, are converted into new substances simpler in composition. The change takes place under the influence of a nitrogenous body called a ferment, which is itself at the same time decomposed. The change is accompanied by the development of minute living organisms, which are now generally supposed to be the cause of the change, and the products, of course, differ with the nature of the fermented body and of the ferment. Most of the living organisms are vegetable growths.

The circumstances necessary for the growth of the ferment are: (a) Proper food, especially the ammoniacal salts and alkaline phosphates. These are generally present in the liquid about to be fermented. (b) A temperature from 60° to 100° F. (20° to 40° C.). Very strong solutions of sugar will not ferment. The access of air is necessary.

A so-called spontaneous fermentation takes place in wine, beer, milk and urine, and is regarded as due to the sporules or seeds of living bodies floating in the air. These, dropping into the liquid, propagate themselves, and during the act of growing evolve the products of fermentation. If the liquid be left in contact only with air which has been passed through a red-hot platinum tube, or if the air be simply filtered by passing it through cotton, and the sporules thus prevented from entering, fermentable liquids may be preserved for a long time without undergoing change. A large number of substances, especially those which coagulate albumen, have the power to stop fermentation, and are called anti-zymotics. Among these are boric acid, zinc chloride, mercuric chloride, carbolic acid, alcohol, sulphites, many hydrocarbons, etc.

The principal forms of fermentation are five.

1. The Vinous, producing chiefly Alcohol, C_2H_6O and Carbonic Anhydride, CO_2.

2. The Acetous, producing chiefly Acetic Acid, $C_2H_4O_2$.
3. " Lactic, " " Lactic Acid, $C_3H_6O_3$.
4. " Butyric, " " Butyric Acid, $C_4H_8O_2$.
5. " Mucous, " " Gum and Mannite.

Pasteur believes that the organisms found in fermenting liquids grow and multiply at the expense of the fermenting body. Liebig thought that the decomposition going on in the ferment was communicated by contact to other substances. He applied the phrase "example" to this action. The theories of fermentation have been extensively discussed in connection with the now popular ideas that most fevers and contagious diseases are caused by living organisms.

PUTREFACTION is a change which bodies containing nitrogen, especially organized bodies, undergo when exposed to air. They are usually converted into simpler products, some of which have characteristic and offensive odors. It differs from fermentation in the fact that it is not due to the presence of any special causative body or ferment; it is in the ordinary sense spontaneous, and the products also are usually more offensive, due in part to the sulphur and phosphorus sometimes present in organized tissues. In putrefaction, numerous living organisms are produced, and the process is interfered with by many substances and circumstances. Many of the anti-zymotics, for instance, act in this way, so does very high or very low temperature, or entire exclusion of all air, except that which has been heated. Bodies which prevent putrefaction are called *antiseptics*.

DECAY. This is the decomposition of organic bodies by the slow action of oxygen. It takes place too slowly for any increase of temperature to be noticed, and it is rarely complete, that is, some portions of the elements escape action. When wood burns with a flame it leaves nothing but the incombustible mineral matter or ash, but when it decays a brown powder is left, which contains some of the original carbon and hydrogen. Decay requires the access of air, the presence of moisture and a temperature above the freezing point.

Organic Substitution. This is a process by which one or more atoms of a body are removed and their place occupied by an equivalent number of atoms of some other element. The atoms replace one another strictly according to the laws of atomicity. Hydrogen is the element which is most commonly thus substituted, but the other elements are subject to similar replacements. Numerous substitution compounds are described further on; it will be sufficient here to outline the general principles of their formation.

1. *Substitution by oxygen.* Oxygen generally substitutes hydrogen; at least two atoms of oxygen are required, one to combine with the liberated hydrogen and the other to take its place. Thus alcohol, when exposed to oxidation, gives the following reaction :—

<div align="center">Alcohol.   Acetic acid.</div>

$$C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$$
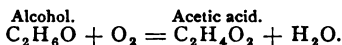
The bodies produced by oxygen substitutions are usually acids.

2. *Substitution by chlorine.* Chlorine usually substitutes hydrogen; one atom of chlorine takes the place of one atom of hydrogen, but the hydrogen thus set free combines with an atom of chlorine; so for the complete reaction two atoms of the latter are needed. Thus :—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$
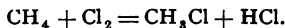
If further substitution occurs it will take place in a similar manner.

$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl.$$
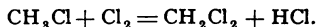
These reactions are generally obtained by the direct action of chlorine on the organic body. Proceeding in this way, we finally reach complete removal of the hydrogen and the formation of CCl_4. This method of substitution is almost the only means we have of forming compounds between carbon and chlorine.

Bromine and iodine follow substantially the same law, but do not act so readily.

3. *Substitution by sulphur.* Sulphur substitutes oxygen, atom for atom, but only a comparatively small number of such substitution compounds are as yet known. They are usually of very marked odor. As an example of a sulphur substitution we have C_2H_6S, which corresponds to alcohol C_2H_6O.

4. *Substitution of NO_2.* This is a substitution for hydrogen, and is the result of the action of strong nitric acid. Each molecule of NO_2 replaces one atom of H. The bodies thus formed are called nitro-compounds, the prefixes bi, tri, etc., being used to indicate the presence of two or more molecules of NO_2. The action of nitric acid on benzene results in the formation of nitro-benzene.

$$C_6H_6 + HNO_3 + C_6H_5NO_2 + H_2O.$$
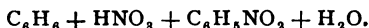
Each molecule of NO_2 substituted requires a molecule of HNO_3. In the production of tri-nitro-glycerin three molecules of HNO_3 are required, thus :—

<div align="center">Glycerin.   Tri-nitro-glycerin.</div>

$$C_6H_8O_6 + 3HNO_3 = C_6H_5(NO_2)_3O_6 + 3H_2O.$$
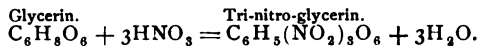
Other substitutions. Nitrogen may, under certain circumstances, be substituted for hydrogen. The bodies so formed are called *azo* compounds.

Silicon may replace carbon, but only a comparatively small number of such instances have been observed.

Organic Synthesis. Until Wöhler prepared urea by heating ammonium cyanate, it was supposed to be impossible to prepare artificially any one of the constituents of animal or vegetable secretions. Although this discovery broke down, to a certain extent, the distinction between organic and inorganic chemistry, yet it long remained nearly alone as a demonstration of the fact. Within twenty-five years past great advances have been made in the work of producing organic bodies artificially, either directly from mineral substances, or from other organic bodies. These methods are called *organic synthesis.* Some of them are highly ingenious, and throw much light on the molecular structure of the bodies concerned. A few instances are given.

Ethyl alcohol, which is generally the result of the natural operation of fermentation, can be prepared directly from its elements in the following manner: Electrical discharges are passed from carbon points through hydrogen gas, by which C_2H_2 is formed, which can be converted into C_2H_4, olefiant gas. This, on being agitated for a long time with water, combines in the following manner and produces alcohol :—

$$C_2H_4 + H_2O = C_2H_6O.$$
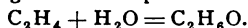
Formic acid, which is a natural secretion, may be made artificially by the action of carbon monoxide on potassium hydroxide.

$$KHO + CO = KCHO_2.$$
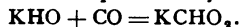
Many other instances of this kind of synthesis are known. Instances of the production of natural products by the transformation of other natural roducts are very numerous, and some of them are of the greatest practical importance. One of these is the manufacture of the coloring matter of madder, a valuable vegetable dye, from anthracene, an otherwise useless ingredient of coal tar. The reactions are as follows :—

Anthraquinone, $C_{14}H_8O_2$, is obtained by the action of a powerful oxidizing agent, as chromic acid, upon the anthracene.

$$C_{14}H_{10} + O_3 = C_{14}H_8O_2 + H_2O.$$
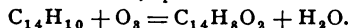
The anthraquinone being heated with bromine gives—

Dibromanthraquinone.
$$C_{14}H_8O_2 + Br_4 = C_{14}H_6Br_2O_2 + 2HBr.$$
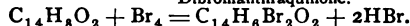
Dibromanthraquinone heated with potassium hydroxide gives potassium alizarate from which the alizarin may be obtained by sulphuric acid.

Potass. alizarate.
$$C_{14}H_8Br_2O_2 + 4KHO = C_{14}H_6K_2O_4 + 2KBr + 2H_2O.$$

Alizarine.
$$C_{14}H_6K_2O_4 + H_2SO_4 = K_2SO_4 + C_{14}H_8O_4.$$
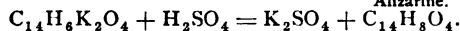
Empirical and Rational Formulæ. When formulæ are written so as to express merely the number of atoms of each element, without attempting to show the arrangement or the relations of the body, we have what are called *empirical formulæ*. When, in addition to expressing the composition, we endeavor, by the arrangement of the symbols, to express the manner in which the molecules are formed and the relation it has to other bodies, we have *rational formulæ*. Thus, alcohol may be represented empirically as C_2H_6O, but many of the changes which alcohol undergoes indicates that one of its atoms of hydrogen is closely associated with the oxygen, while the other hydrogen atoms are more closely associated with the carbon. Accordingly, the formula C_2H_5HO is used to indicate this arrangement. A perfect rational formula should indicate how the body is formed and all the changes to which it tends, but such formulæ are not yet possible to us. Alcohol, for instance, can be formed by the combination of a body called ethene, C_2H_4, with water, H_2O, and to represent this fact we might write the formula $C_2H_4H_2O$, but this would conflict with the formula just given. We might combine the two formulæ by writing $C_2H_4H\ H\ O$, but this would be rather complicated. In a large number of organic compounds the rational formulæ are not known.

Percentage Composition. The results of analysis may be expressed without any reference to symbols, or to the number of atoms of the elements present. We may give simply the number of *parts by weight* of each element contained in *one hundred parts* of the body. Thus the composition of ordinary sugar may be stated as:—

Carbon 41.98
Hydrogen... 6.43
Oxygen... 51.59
———
100.00

These figures represent the *percentage composition*.

Isomerism, Metamerism and Polymerism. Many instances are known, especially in organic chemistry, of two or more bodies entirely different in origin and character, having the same percentage composition. Acetic acid, lactic acid and glucose all have the composition:—

Carbon 40
Hydrogen... 6.66
Oxygen 53.34
———
100.00

Similarly, the composition of the bodies known respectively as methyl acetate, ethyl formate and propionic acid have the same composition.

This relation is known as *isomerism*, and if we compare the formulæ of isomeric bodies they fall naturally into two classes, 1st, those that agree both in number of atoms and molecular weight; 2d, those that differ in number of atoms and molecular weight. The compounds methyl acetate, ethyl formate and propionic acid form a series of the first class, while acetic acid, lactic acid and glucose are examples of the second.

	Empirical Formulæ.	*Rational Formulæ.*	*Mol. Wt.*
Methyl acetate........................	$C_3H_6O_2$	$CH_3C_2H_3O_2$	74
Ethyl formate........................	$C_3H_6O_2$	$C_2H_5CHO_2$	74
Propionic acid	$C_3H_6O_2$	$HC_3H_5O_2$	74

It will be seen that the rational formulæ are very different, but as far as actual number of atoms is concerned each body is identical. Such a relation is said to be one of metameric isomerism or *metamerism*. In the other case referred to we have :—

	Empirical Formulæ.	*Rational Formulæ*	*Mol. Wt.*
Acetic acid...........................	$C_2H_4O_2$	$HC_2H_3O_2$	60
Lactic acid...........................	$C_3H_6O_3$	$HC_3H_5O_3$	90
Glucose	$C_6H_{12}O_6$	Unknown	180

Here the only agreement is in percentage composition. Such a relation is called *polymeric isomerism*.

Isomeric modification. A special form of isomerism is where two or more bodies are identical in composition and molecular weight, and so nearly alike in properties and reactions as to indicate that they are forms of the same body, but each is under a slight modification. Thus five modifications of the substance called pentyl alcohol ($C_5H_{12}O$) have been described. Each one of these differs slightly from the others in boiling point, action on light, etc , but they are evidently all entitled to the name pentyl alcohol.

These are more intimate relations than ordinary isomerism, and can best be explained by supposing that certain minor differences exist in the molecule, particularly with reference to the position of the carbon atoms. This theory is explained on a subsequent page.

Determination of the Formulæ of Organic Bodies. The percentage composition of a body gives only an imperfect clue to its formulæ ; to obtain this latter we must know something of the molecular weight. Now, as a general rule, it is found that the molecular weight is equal to twice the density of the body in state of vapor compared to hydrogen. The

determination of the *vapor density* becomes, therefore, an important operation. It may be accomplished in two ways: 1st. Placing some of the substance in a flask of known weight, heating the flask sufficiently to convert the body entirely into vapor, then sealing and re-weighing the flask. The difference between the two weights gives the weight of the vapor. The capacity of the flask is then estimated, and thus the weight of a known volume of vapor is determined. Corrections have to be made for temperature and pressure, and other sources of error. 2d. The vapor density may also be estimated by introducing a given weight of the substance into a graduated tube filled with mercury, and then converting the whole of the substance into vapor, and measuring the volume. As the weight and volume are thus both known, the density can be calculated. The use of these determinations of vapor density is shown by the following example. The composition of alcohol might be represented by the formulæ C_2H_6O, $C_4H_{12}O_2$, or any other multiple, because the *proportion* between the elements would remain the same. The vapor density is, however, found to be 23, and since, by the rule above given, the vapor density is half the molecular weight, such a formula must be chosen as shall give a molecular weight of 46. The one which will give this is :—

$$
\begin{array}{rl}
C_2 & = 24 \\
H_6 & = 6 \\
O & = 16 \\
\hline
& 46
\end{array}
$$

C_2H_6O is, therefore, the correct formula for alcohol.

Homologous and Isologous Series. In many cases, when the formulæ of organic bodies, similar in some properties, are arranged in order, they will be found to differ by a regular rate, the carbon increasing or diminishing by one atom and the hydrogen by two. The result is a series of bodies differing by CH_2. Such a series is called a *homologous* series; when the carbon remains the same, but the hydrogen differs by H_2, the series is said to be *isologous*.

In the following examples each vertical column represents a homologous, each horizontal line an isologous series :—

$C\ H_4$	$C\ H_2$	C
C_2H_6	C_2H_4	C_2H_2
C_3H_8	C_3H_6	C_3H_4
C_4H_{10}	C_4H_8	C_4H_6
C_5H_{12}	C_5H_{10}	C_5H_8

General Formulæ. The existence of these homologous series, as above described, renders it possible to express by a single formula the composition of any member of the group. Thus, in the first series, the atoms of hydrogen are always two more than twice the carbon atoms; in its next series the atoms of hydrogen are just twice the carbon; in the third series the hydrogen atoms are two less than twice the carbon atoms. For the first series we could give, then, the general formula $C_n H_{2n+2}$; n represents any number of atoms. From this formula we can derive any member of the series; for instance, let it be required to write the formula of the sixth member. As the carbon increases regularly one atom at a time, the sixth member will have six carbon atoms, therefore C_6. Twice six plus two is fourteen; the formula is therefore $C_6 H_{14}$. The general formula of the second series above given is $C_n H_{2n}$; of the third series $C_n H_{2n-2}$.

Carbon Skeletons or **Duplication of Carbon.** The valency or combining capacity of each member of a homologous series is the same. It is not difficult to understand how this is, as far as regards the first member of the series, but at first sight it would seem as if each member should have a different valency. Thus, if CH_4 is a saturated molecule, $C_2 H_6$, a homologue with it, would seem to be a dyad; for carbon being a tetrad, two of carbon would have a capacity of eight; six would be saturated by the H_6, leaving two unsatisfied. Experiment, however, shows that $C_2 H_6$ is not a dyad, but a saturated molecule, and so with all bodies homologous with it. The explanation of this fact is upon the supposition that, in forming the molecules, the carbon has in part satisfied itself, so that each atom of carbon added carries into the molecule only two degrees of valency, which the H_2, added at the same time, immediately satisfies. This explanation cannot be made clear without the use of diagrammatic

formulæ. Thus the first member of the series would be

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\vert}}\!\!\overset{\vert}{C}\!\!\underset{\vert}{\vert}-H\text{; the}$$

second member would have the carbon partly satisfying itself, thus:

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\vert}{C}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\vert}{C}}}-H\text{, the molecule then being saturated. The third would}$$

$$\begin{array}{ccc} H & H & H \\ | & | & | \\ \end{array}$$

be H—C—C—C—H, and so on with each member. We might give

$$\begin{array}{ccc} | & | & | \\ H & H & H \end{array}$$
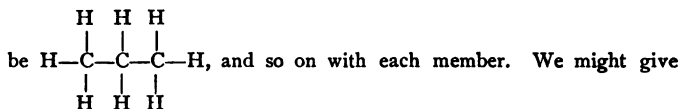
names to the linked carbon atoms—or carbon skeletons, as they have been ingeniously called—calling them di-carbon, tri-carbon, etc.

Properties of Bodies in Homologous Series. The relation of homologous bodies is not a mere accidental relation in formulæ. By comparing different members of the same series we can always see similarities either in origin, general properties or chemical relation. The series beginning with CH_4 is remarkable for general indifference to chemical action. The series beginning with CH_3 is remarkable for the fact that their hydroxides constitutes a series of alcohols which possesses specific physiological action. In each series the fusing and boiling points, specific gravity, density of vapor, increase with considerable regularity. The molecular weight, of course, increases, but in the series beginning with CH_2 the percentage composition is the same in all, and they are, therefore, instances of polymeric isomerism. The molecular weight increases regularly, 14, 28, 42, etc., but the percentage composition is always carbon, 85.71; hydrogen, 14.29. By the density of the vapor we can distinguish each one and determine the formula.

Isomeric Modification in Homologous Series. It has been pointed out, on a previous page, that many organic bodies occur in two or more forms which are not sufficiently distinct to permit us to consider the bodies as different, and yet they are evidently not exactly identical. In such cases the diagrammatic method of showing the linking of the carbon atoms may be utilized to show that the difference of properties in two or more forms of the same body may be due to different positions of the carbon atoms, with respect to each other and to the other elements present. In the lower members of the series, on account of the small number of atoms present, it is generally impossible to make more than one arrangement; but in the higher members several different arrangements are possible, and each arrangement will have certain characteristic indications, either in the chemical or physical properties of the bodies formed. In the series beginning with CH_4 no variation of arrangement can be made in the carbon atoms in the first three members, but in the fourth member tetrane, C_4H_{10}, we may have no carbon atom united to more than two other carbon atoms, or we may have one carbon

First Form.

$$H-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-H$$

or $CH_3CH_2CH_2CH_3$

Second Form.

$$H-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-H$$

$$H-\overset{\displaystyle |}{C}-H$$

or $CH_3CH(CH_3)CH_3$
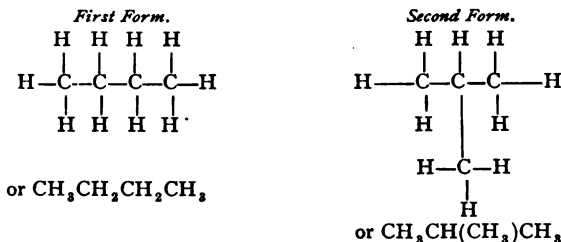
In the second compound, the CH_3, which stands rather apart from the remainder of the molecule, may be regarded as a substituting molecule; and the number of isomeric modifications of which any body is susceptible will depend on the number of points at which the substitution can take place. We might formulate the two forms of tetrane very simply thus:—

C_4H_{10}, ordinary tetrane $C_3H_7(CH_3)$, methyl tetrane.

The distinction between such isomeric modifications may often be obtained by determining the substances produced, when the different bodies are subjected to the same decomposing influences.

Classification of Organic Bodies. No system of classification of organic bodies is entirely satisfactory. The following is an outline of the classification adopted in this volume:—

Hydrocarbons (bodies containing C and H).
Derivatives from the hydrocarbons.
Alcohols.
Ethers.
Aldehydes.
Acids.
Sugars and starches.
Oils and fats.
Compounds containing nitrogen.
Cyanogen derivatives.
Ammonium derivatives.
Natural alkaloids.
Animal and vegetable chemistry.

HYDROCARBONS.

The compounds of carbon and hydrogen are very numerous. Carbon being a tetrad, the highest quantity of hydrogen which could combine with carbon is four atoms. In the compound CH_4 we have the type of the

hydrocarbons; all other compounds of this class might be regarded as derived by subtraction or substitution, or both.

If we substitute in CH_4 for all or part of the hydrogen its equivalent of any other substance, we will not disturb the chemical nature; it was a saturated hydrocarbon, and remains so. Hence CCl_4 will be referable to the same group as CH_4. By successive subtractions of H from CH_4 we may obtain a series of unsaturated molecules, the valency of which will be equal to the number of hydrogen atoms removed. CH_3 lacks one atom of H; it is a monad *radicle;* CH_2 is a dyad, CH a triad, while C, of course, is a tetrad. From each of the intermediate molecules—hydrocarbon radicles they are called—derivatives may be obtained, comparable in the main to the derivatives which the elements themselves yield. Thus, from CH_3, may be obtained a chloride, bromide, hydroxide, sulphate, etc., analogous in formulæ to the same compounds formed by the elements of the potassium group. From CH_2 compounds may be obtained analogous in formulæ to those from dyad metals, and so on. In addition, these radicles have substitution power, that is, they may replace the hydrogen of other organic compounds. Each of these radicles and each of their derivatives may constitute the first member of a homologous series. A system of nomenclature by terminations has been adopted to distinguish the different series; the vowels are used in regular order, and the syllable *yl* indicates uneven valency. The number of carbon atoms is indicated, except in the first two members, by syllables formed from the Greek numerals. The following table will be sufficient to show the principle of the classification:—

Series.	Series.	Series.	Series.	Series.
1	2	3	4	5
Gen. Formula	Gen. Formula	Gen. Formula	Gen. Formula	Gen. Formula
$C_n H_{2n+2}$.	$C_n H_{2n+1}$.	$C_n H_{2n}$.	$C_n H_{2n-1}$.	$C_n H_{2n-2}$.
Valency.	Valency.	Valency.	Valency.	Valency.
0	I	II	III	IV
Methane.	Methyl.	Methene.	Methenyl.	Methine.
CH_4	CH_3	CH_2	CH	C
Ethane.	Ethyl.	Ethene.	Ethenyl.	Ethine.
C_2H_6	C_2H_5	C_2H_4	C_2H_3	C_2H_2
Tritane.	Trityl.	Tritene.	Tritenyl.	Tritine.
C_3H_8	C_3H_7	C_3H_6	C_3H_5	C_3H_4
Tetrane.	Tetryl.	Tetrene.	Tetrenyl.	Tetrine.
C_4H_{10}	C_4H_9	C_4H_8	C_4H_7	C_4H_6
Pentane.	Pentyl.	Pentene.	Pentenyl.	Pentine.
C_5H_{12}	C_5H_{11}	C_5H_{10}	C_5H_9	C_5H_8
Hexane.	Hexyl.	Hexene.	Hexenyl.	Hexine.
C_6H_{14}	C_6H_{13}	C_6H_{12}	C_6H_{11}	C_6H_{10}

It does not necessarily follow that all these bodies have been obtained, but most of them are known, and the others could doubtless be prepared. The members of each vertical column are homologous with each other.

The members of the first series being saturated hydrocarbons, are practically indifferent to chemical agents. Common paraffin is one of them, and the series has, for this reason, been called the *paraffins;* the members of the third series have been called the olefins, from the former name of one of the members of it.

PARAFFINS OR METHANE SERIES.

Saturated molecules not easily affected by chemical agents. Many of them are found in petroleum.

Methane, Marsh Gas, CH_4. This body exists in common coal gas, being formed during the destructive distillation of coal. It is also produced by decay of vegetable matter, especially under water, and hence is frequently found in marshes, whence its name. By stirring the bottom of a marshy pool, bubbles of methane will escape. It can be prepared pure by heating a mixture of sodium acetate and sodium hydroxide.

Sodium acetate.
$$NaC_2H_3O_2 + NaHO = Na_2CO_3 + CH_4.$$
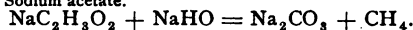
It is a colorless gas, and, except hydrogen, is the lightest body known.

Common Paraffin exists in petroleum and in coal tar. It is a mixture of several of the higher members of the series. It is a white waxy solid, easily fusible, soluble in ether, little acted on by acids or alkalies. It is used for a protecting coating in chemical apparatus, and as a substitute and sometimes as an adulterant for wax. Cosmoline, vaseline and similar substances are also in part soft paraffins.

Derivatives of the Paraffins. These bodies are not very easily acted on by chemical agents, but by substitution, compounds may be obtained by direct action of chlorine, and even bromine, on all of them, and nitro compounds may also be produced directly from some of the higher members. By successive substitution of the hydrogen in CH_4 we get four bodies which may be given as an illustration of the nomenclature of this kind of compounds.

Methane.. CH_4
Monochlorinated methane........................... CH_3Cl
Di   "   "   .... CH_2Cl_2
Tri   "   "   .... $CHCl_3$
Carbon tetrachloride .... CCl_4

The third substitution is the very important body, **Chloroform**, $CHCl_3$. This is not usually obtained by the process just given, but generally by distilling common alcohol with bleaching powder. The reaction is complicated, and the product is at first quite impure. When pure it is a colorless, fragrant liquid, very volatile, specific gravity 1.48, not easy to burn, insoluble in water and much heavier than that liquid. It boils at 142° F. (61° C.), has high solvent powers and is a valuable anæsthetic.

Iodoform, CHI_3, is now much used as an antiseptic, especially in surgery. It cannot be obtained by direct substitution, but is easily made by the action of iodine on a mixture of alcohol and potassium hydrate. It forms bright yellow crystals.

Carbon tetrachloride, CCl_4, is the final result of the substitution of chlorine for the hydrogen of methane, CH_4. It is a colorless liquid of specific gravity 1.56, freezes at —9° F. (—23°C.), and boils at 172° F. (77° C.). It is a powerful anæsthetic.

METHYL SERIES.

This is a series of monad radicles which are usually called the alcohol radicles because their hydroxides are the common alcohols. The radicles themselves are of but little importance, but their known compounds are very numerous and include some of the most important organic bodies. In the free state the radicles exist as double molecules. Free methyl for instance is $(CH_3)_2$.

Derivatives from the Methyl Series.

Normal oxides, called ETHERS.

$(CH_3)_2O$ Methyl ether, analogous to Na_2O, sodium oxide.
$(C_2H_5)_2O$ Ethyl ether,   "   "   "   "
Compounds with halogens, sometimes called ETHERS.
$(CH_3)Cl$ Methyl chloride, analogous to NaCl, sodium chloride.
$(C_5H_{11})Cl$ Amyl,   "   "   "   "   "
Compounds derived from acids, called COMPOUND ETHERS or ESTERS.
$(CH_3)_2SO_4$ Methyl sulphate, analogous to Na_2SO_4, sodium sulphate.
$(C_5H_{11})NO_3$ Amyl nitrate,   " $NaNO_3$, sodium nitrate.
The compounds analogous to the acid salts are sometimes called VINIC ACIDS.

$(C_2H_5)HSO_4$ Sulphethylic acid, analogous to $KHSO_4$.
$(C_5H_{11})HSO_4$ "   amylic "   "   "

Hydroxides, called ALCOHOLS.

$(C_2H_5)HO$ Ethyl alcohol, analogous to KHO.

$(C_5H_{11})HO$ Amyl   "   "   "

Compounds containing two different radicles, called MIXED ETHERS.

$(CH_3)(C_2H_5)O$ Methyl ethyl ether.

Chlorides, bromides, hydrides, etc., are known, and many substitution compounds.

As in these different compounds the proportion of carbon is not affected; and if the proportion of hydrogen is affected it will be equally affective on all the members of the series; it is obvious each one of the sets of compounds here mentioned will constitute a homologous series.

In general, when alcohols are oxidized by a limited amount of oxygen, two atoms of hydrogen are removed and no oxygen is added. When oxidized in a free supply of oxygen, an atom of oxygen takes the place of the removed hydrogen. The bodies produced in the first case are aldehydes, in the second, acids. In this way we have—

$$\underset{\text{alcohol.}}{\overset{\text{Methyl}}{(CH_3)HO}} + O = \underset{\text{aldehyde.}}{\overset{\text{Methyl}}{CH_2O}} + H_2O.$$

$$(CH_3)HO + O_2 = \overset{\text{Formic acid.}}{CH_2O_2} + H_2O.$$
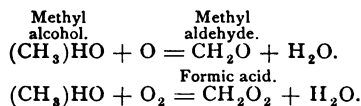
Thus each alcohol may be made to yield an aldehyde and an acid, each of these forming part of a homologous series.

The series of acids is very important; many of them exist in fats and oils, hence they have been called fat acids. The following table gives a conspectus of some of the most important derivations of the methyl series of hydrocarbons. It will be noticed that in the series of aldehydes and acids the radicles are not indicated. The hydrogen that is removed in producing these bodies appears to come from the radicle. Of the hydrogen that remains in the acid one atom is replaceable by any positive element or radicle, so that we generally write these acids, $HCHO_2$, formic acid. Further explanation of the constitution, etc., of these acids is given on a later page. In the table on the next page only a few examples of the compound ethers are given.

C

Radicle.	Oxides, ethers.	Hydroxides, alcohols.	Aldehydes.	Acids.	Acid sulphates, vinic acids.	EXAMPLES OF COMPOUND ETHERS Sulphates.	Nitrates.
CH_3	$(CH_3)_2O$	CH_3HO	CH_2O	CH_2O_2	CH_3HSO_4	$(CH_3)_2SO_4$	CH_3NO_3
C_2H_5	$(C_2H_5)_2O$	C_2H_5HO	C_2H_4O	$C_2H_4O_2$	$C_2H_5HSO_4$	$(C_2H_5)_2SO_4$	$C_2H_5NO_3$
C_3H_7	$(C_3H_7)_2O$	C_3H_7HO	C_3H_6O	$C_3H_6O_2$	$C_3H_7HSO_4$	$(C_3H_7)_2SO_4$	$C_3H_7NO_3$
C_4H_9	$(C_4H_9)_2O$	C_4H_9HO	C_4H_8O	$C_4H_8O_2$	$C_4H_9HSO_4$	$(C_4H_9)_2SO_4$	$C_4H_9NO_3$
C_5H_{11}	$(C_5H_{11})_2O$	$C_5H_{11}HO$	$C_5H_{10}O$	$C_5H_{10}O_2$	$C_5H_{11}HSO_4$	$(C_5H_{11})_2SO_4$	$C_5H_{11}NO_3$

Isomeric modifications are possible in these bodies, except in the first two lines, i. e., methyl ethyl, and their derivatives.

Methods of Forming the Compounds of the Methyl Series. The starting point is generally the alcohols. The ethers, simple and compound, are produced by the action of acids on the alcohols. The aldehydes are produced by partial oxidation, the acids by complete oxidation ; most of the acids exist ready formed in nature.

The alcohols will be described first. They are often called the monatomic alcohols, because they contain a monatomic radicle.

CONSPECTUS OF KNOWN MONATOMIC ALCOHOLS.

Systematic Names.	Common Name.	Sp. Gr. approx.	Boil. Pt.		Source.
			F.	C.	
Methyl.	Wood Spirit	0.798	151	66.1	Distillation of wood.
Ethyl.	Alcohol	0.793	173	78.3	Fermentation.
Trityl.	Propyl Alcohol	0.820	206	96.6	"
Tetryl.	Butyl "	0.803	233	112	"
Pentyl.	Amyl " Fusel Oil	0.811	270	132	"
Hexyl.	Caproic Alcohol	0.819	309	154	"
Heptyl.	Œnanthic "		343	173	Action of KHO on Castor oil.
Octyl.		0.871	356	80	From parsnip oil.
Nonyl.			392	200	
Decyl.	Rutic "		414	212	Oil of Rue; fuses at 44.5° F. (7° C.).
Dodecyl.	Lauric "				Whale Oil; fuses at 75° F. (24° C.).
Tetradecyl	Myristic "				
Hexadecyl	Cetyl				Spermaceti; fuses at 122° F. (90° C.).
Octadecyl	Stearic "				From Stearic Acid; fuses at 138° F. (59° C.).
	Cerylic "				Chinese Wax; fuses at 174° F. (78° C.).
	Melissic "				Beeswax; fuses at 185° F. (85° C.).

Methyl Alcohol, wood spirit, $(CH_3)HO$, **methyl hydroxide,** is usually made by distilling wood. The crude material is difficult to purify. True methyl alcohol is colorless, and of pleasant odor. It boils at 152° F. (66.5° C.), and its effects on the animal system appear to be less severe and more transient than those of common alcohol. The methylated spirit of English chemists is a mixture of 90 parts common alcohol with 10 parts methyl alcohol.

Ethyl Alcohol, common alcohol, spirit of wine, $(C_2H_5)HO$, **ethyl hydroxide,** is produced in the vinous fermentation of sugar, alcohol and carbonic anhydride being chiefly formed; it can also be prepared artificially. On the large scale the sprouted grain called malt is generally used. The general nature of the fermentation is explained in connection with the sugars. The fermented spirit is concentrated by distillation, but the strongest spirit thus prepared contains between five and ten per cent. of water. To withdraw all the water, it is necessary to distill with quick-

lime or calcium chloride, by which *absolute alcohol* is formed. This is inflammable, absorbs water and mixes with it in all proportions.

Proof-spirit contains 50.8 parts by weight of absolute alcohol to 49.2 of water, and has a specific gravity of 0.920. Commercial alcohol is a colorless volatile liquid, of which the properties, effects and uses are well known. The strongest spirit ordinarily furnished is about 95 per cent., and boils at about 180° F. (81° C.). Alcohol is contained in wine, beer and spirits, certain essential oils, sugars, or extracts being employed as flavoring agents. Whisky, brandy, and other spirits contain from 40 to 50 per cent. of alcohol; wines, from 17 (port and madeira) to 7 or 8 (hock and light clarets) per cent.; porter and strong ale contain from 6 to 8 per cent.; lager beer about 4 per cent. The effervescence of fermented liquids is due to the carbon dioxide which is produced with the alcohol, thus :—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} \text{ breaks up into } \underset{\text{Alcohol.}}{2C_2H_6O} + 2CO_2.$$
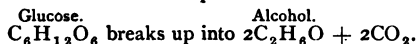
The carbon dioxide is retained by bottling the liquid before the fermentation is over.

The chemical character and adulterations of alcoholic beverages are discussed in the chapter on food.

Pentyl Alcohol, Fusel Oil, $(C_5H_{11})HO$. The radicle C_5H_{11} has been called amyl, and this alcohol is generally known as amyl alcohol. It is a by-product in fermentation, and is found in raw spirits and new liquors. When pure it is a colorless oily liquid, with a peculiar odor, a hot and acrid taste, and decidedly poisonous in its action.

The alcohols derived from the higher radicles are mostly wax-like.

Isomeric forms of alcohol. Methyl and ethyl alcohols present only one form, but a number of isomers of the higher alcohol have been obtained. Comparison of these isomers has led to their division, according to a supposed arrangement of the carbon atoms, into three groups, primary, secondary and tertiary alcohols. These forms are distinguished by the different results of the action of oxygen on them.

ETHERS.

The primary alcohols, by the action of bodies which have an affinity for water (sulphuric and phosphoric acids), are converted into oxides, called ethers. If free acids are present when the ether is being formed, the two bodies will generally act on one another producing a *compound ether*, which is merely the replacement of the hydrogen of the acid by one or *more* molecules of the radicle. The only simple ether of any importance *is* ;—

Ethyl Oxide Ether, $(C_2H_5)_2O$, often wrongly called sulphuric ether, usually made by the action of sulphuric acid upon alcohol. It appears that acid ethylsulphate is first formed and then decomposed.

$$\overset{\text{Alcohol.}}{(C_2H_5)HO} + H_2SO_4 = \overset{\text{Acid ethylsulphate.}}{(C_2H_5)HSO_4} + H_2O.$$
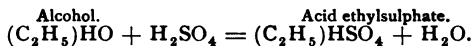
Another molecule of alcohol is then acted upon, thus :—

$$(C_2H_5)HO + (C_2H_5)HSO_4 = H_2SO_4 + \overset{\text{Ether.}}{(C_2H_5)_2O}.$$
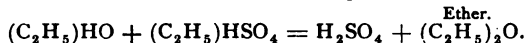
Ether is a colorless, very volatile liquid, of distinct odor, boiling at 98° F. (37° C.). Specific gravity 0.723. Its vapor is inflammable and very heavy. It is a solvent for fats, fixed and volatile oils, resins and many other proximate principles. Its anæsthetic uses are well known.

Compound Ethers. These are, of course, very numerous. Many of them have marked odor and are the flavoring materials of flowers and fruits. They can mostly be made artificially, and various mixtures of them are extensively used for imitating various flavors. Some that are the more important will be described in connection with the organic acids with which they are prepared. The compound ethers formed with inorganic acids are not very important, but a few have come into notice.

Ethyl Bromide, $C_2H_5Br.$, is an anæsthetic.

Ethyl nitrite, $C_2H_5NO_2$, is a product of the action of nitric acid on alcohol, and is one of the ingredients of the old remedy known as sweet spirit of nitre.

If urea be added to the mixture of alcohol and nitric acid the formation of a nitrite is prevented and we get *ethyl nitrate*, $C_2H_5NO_3$.

Pentyl nitrite, $C_5H_{11}NO_2$, often called amyl nitrite, is made by the action of nitric acid upon pentyl (amyl) alcohol. It is a yellowish liquid, of well marked odor, boiling at 205° F. (96° C.). It has a powerful action on the circulation of the brain, and is used for this effect in medical practice.

ORGANO-METALLIC DERIVATIVES.

Many of the hydrocarbons are capable of uniting with those elements which are commonly called metals, to form bodies which are sometimes themselves capable of acting as radicles. They are called organo-metallic bodies. Among them are zinc ethyl, $Zn(C_2H_5)_2$, and arsen-dimethyl $As(CH_3)_2$. The latter is a radicle called *kakodyl*, and forms a large number of compounds, most of them poisonous. One, however, kakodylic acid, $As(CH_3)_2HO_2$, although over half its weight arsenic, is not poisonous.

By the action of potassium or sodium upon alcohols, the hydrogen that not part of the radicle is expelled, and bodies having some of the properties of caustic alkalies are obtained. Thus, with sodium and common alcohol, the reaction is:—

$$C_2H_5HO + Na = C_2H_5NaO + H.$$
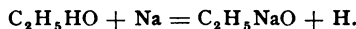
C_2H_5NaO is called *sodium ethylate;* it is a caustic liquid, which has lately been introduced in use in surgery as an escharotic.

SULPHUR ALCOHOLS, MERCAPTANS.

The oxygen of organic bodies, as of inorganic bodies, may be replaced by any other element of the oxygen group. Ethyl alcohol, for instance, has a corresponding sulphur compound, C_2H_5HS, which has been given the somewhat fanciful name of *mercaptan;* its proper name is ethyl hydrosulphide. Corresponding ethers also are known; thus, $(C_2H_5)_2S$, ethyl sulphide. These sulphur derivatives are most strong smelling and irritative compounds. A few of them exist ready-formed in the secretions of animals and plants. The essential oils of mustard and garlic are sulphur compounds, and are noticed elsewhere.

ALDEHYDES.

These are the results of the removal of two atoms of hydrogen from the alcohols, and stand intermediate between these and the acid. As a group they have little importance. *Ethyl aldehyde*, often called *acetic aldehyde*, or simple *aldehyde*, C_2H_4O, is often present in liquors, especially in raw forms of commercial spirits, and probably gives to such articles some of their injurious qualities. It is a colorless, volatile, acid liquid, lighter than water, and boiling at 70° F. (21° C.), having a powerful affinity for oxygen, and therefore a reducing action. It presents several isomeric modifications, one of which, *paraldehyde*—to which the formula $C_6H_{12}O_3$ has been assigned—has decided narcotic properties, and has lately been used as a substitute for morphia, etc. All the aldehydes of this series form numerous complicated compounds of great chemical interest, but as yet of no practical value.

Chloral. By substituting three atoms of hydrogen in ethyl aldehyde, by chlorine, we obtain a colorless liquid heavier than water (specific gravity 1.8), and boiling at 201° F. (94° C.). This is chloral, C_2HCl_3O. It combines with one molecule of water to form a crystalline, pungently smelling solid, which is now extensively used as a narcotic under the *name of chloral hydrate.* It was originally suggested for this purpose on

account of the decomposition which it undergoes in alkaline solutions, as shown in the following reaction:—

| | Sodium | Sodium | |
| Chloral. | hydroxide. | formate. | Chloroform. |

$$C_2HCl_3O + NaHO = NaCHO_2 + CHCl_3.$$
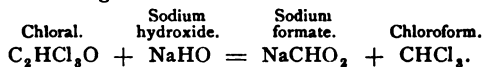
It was supposed that this reaction would occur in the blood, and thus the sedative action of chloroform be secured. Chloral hydrate is quite soluble in water, is an antiseptic, and answers very well for preserving anatomical specimens, urine and other decomposable material.

KETONES.

By the destructive distillation of calcium acetate a body called acetone, C_3H_6O, is formed. It will be seen that this formula differs from that of aldehyde, C_2H_4O, by CH_2. It may be regarded as aldehyde, in which one atom of hydrogen is replaced by CH_3, thus:—

| Aldehyde. | Acetone. |
| C_2H_4O | $C_2H_3(CH_3)O$ |

Acetone is the type of a group known as the *ketones*, which are products of the various reactions, for instance, of destructive distillation.

When secondary alcohols are oxidized they yield a ketone instead of an acid, and when a ketone is oxidized it forms two acids, while an aldehyde forms only one.

FAT-ACIDS.

This term, applicable strictly to only a few of the series, will suffice to distinguish the homologous bodies derived from the alcohols by substitution of two atoms of hydrogen by one atom of oxygen. They form an extensive and important class; nearly all of them are natural products. The fused oils and fats contain some of the higher members of the series. Some have been produced artificially by a reaction, of which the following is a type :—

| Ethyl alcohol. | Acetic acid. |
| $C_2H_6O + O_2 = C_2H_4O_2 + H_2O.$ | |
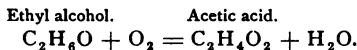
Each of the acids so produced contains but one atom of hydrogen, which can be replaced by a positive element or radicle, and it is usual to designate this fact by writing the formula with one atom of hydrogen separated from the others, as shown in the following table. The lower members of the series are freely soluble and miscible with water, strongly acid and irritative, but as the quantity of carbon and hydrogen increases these bodies become more and more oily, and the higher members are distinctly fatty, feebly acid, insoluble in water, but soluble in alcohol and ether.

HOMOLOGOUS SERIES OF FAT-ACIDS.

Common name.	Formula.	Melting Point.		Boiling Pt.		Properties.	Natural Occurrence.
		F.	C.	F.	C.		
Formic........	$HCHO_2$	34	1	212	100	Colorless volatile liquid.	In red ants and some other insects, and in some stinging plants.
Acetic.........	$HC_2H_3O_2$	62	17	246	119	Colorless pungent liquid.	Slow oxidation of alcohol and sugar. Also ready formed in animals and plants.
Propionic	$HC_3H_5O_2$	62	17	256	141	Crystalline solid.	
Butyric	$HC_4H_7O_2$	—4	—20	322	161	Colorless liquid of disagreeable odor.	Butter and other animal secretions.
Valeric........	$HC_5H_9O_2$			347	175	Colorless liquid of disagreeable odor.	Valerian root.
Caproic	$HC_6H_{11}O_2$	41	5	388	198	Colorless oily body.	Butter and coco-nut oil.
Œnanthylic..	$HC_7H_{13}O_2$			414	212	Slightly soluble in water; has an agreeable odor.	Oxidation of castor oil.
Caprylic......	$HC_8H_{15}O_2$	57	14	456	236		Butter, coco-nut and castor oils.

HOMOLOGOUS SERIES OF FAT-ACIDS—*Continued.*

Common name.	Formula.	Melting Point.		Boiling Pt.		Properties.	Natural Occurrence.
		F.	C.	F.	C.		
Pelargonic ...	$HC_9H_{17}O_2$	64	18	500	260	Crystalline solid.	Geranium leaves.
Capric.........	$HC_{10}H_{19}O_2$	86	30	505	270	Crystalline mass having the odor of sweat.	Butter and coco-nut oil. Fusel oil.
Lauric.........	$HC_{11}H_{21}O_2$	110	44			Silky crystals.	In coco-nut oil.
Myristic	$HC_{14}H_{27}O_2$	129	54			Crystalline scales.	In nutmeg and coco-nut oil.
Palmitic	$HC_{16}H_{31}O_2$	143	62			Fat-like solid.	Most natural fats.
Margaric......	$HC_{17}H_{33}O_2$	140	60			" "	Resembles palmitic. There has been some doubt as to the identity of this acid.
Stearic.........	$HC_{18}H_{35}O_2$	156	69			" "	Most natural fats.
Arachidic	$HC_{20}H_{39}O_2$	167	75			White, crystalline, fatty solid.	Peanut oil.
Behenic........	$HC_{22}H_{43}O_2$	168	76			" " "	Oil of ben.
Hyenic.........	$HC_{25}H_{49}O_2$	171	77			Resembles Cerotic.	
Cerotic	$HC_{27}H_{53}O_2$	172	78			Crystallizes in small grains.	Free in beeswax, and combined in the vegetable fat known as Chinese wax.
Melissic	$HC_{30}H_{59}O_2$	190	88				Derived from beeswax.

Although one of the most complete lists of homologous bodies we have, yet, as will be seen by the table, a few of the members have not been obtained. In the case of each acid described below, reference to the method of preparation by oxidizing the corresponding alcohol is considered unnecessary. The compounds with the organic radicles are shown in tabular form at the end of the description of the acids and their common salts.

Formic Acid, $HCHO_2$, originally prepared from the red ant (Formica rufa), can be made by a number of methods, among which are, heating oxalic acid, oxidation of gum, sugar or starch, action of potassium hydroxide on carbon monoxide, and on chloral. The last two methods, interesting as examples of organic synthesis, are referred to elsewhere. Formic acid is a powerful reducing agent, blisters the skin and is remarkable as having nearly the same boiling and freezing point as water (see table). The formates are all soluble in water.

Acetic Acid, $HC_2H_3O_2$. This occurs in small quantities in animal and plant juices. In the dilute form it constitutes vinegar, which contains about 5 per cent. of the acid, and is usually made by oxidizing dilute alcohol in the presence of a ferment. Acetic acid is also produced in the distillation of wood, being in this case generally contaminated with tar and called pyroligneous acid. When pure, it is a colorless, corrosive liquid, solidifying at 62.6° F. (17° C.), and boiling at 246° F. (119° C.). This is glacial acetic acid. The dilute forms are less active, and in vinegar its effects are quite mild.

ACETATES. The most important of these are :—

Sodium acetate, $NaC_2H_3O_2$, which form deliquescent crystals, containing $3H_2O$. It is largely used in the laboratories for separating iron in analytical work.

Ammonium acetate, $(NH_4)C_2H_3O_2$, is used in medicine in the form of a solution in water called spirit of Mindererus.

Lead acetate, $Pb(C_2H_3O_2)_2$, *sugar of lead,* made by dissolving lead monoxide in acetic acid, forms white crystals, soluble in water. By boiling this solution with lead monoxide, a considerable amount of the latter is dissolved, and the *sub-acetate,* more correctly oxy-acetate, is formed, called Goulard's extract, and when much diluted, lead water. This substance is somewhat unstable and rather uncertain in composition.

Copper acetate, $Cu(C_2H_3O_2)_2$, is not important; but an irregular and variable compound of it with copper hydroxide, known as *verdigris,* is made by exposing alternate layers of sheet copper and refuse grape skins

to the air; ethyl alcohol is formed and then converted into acetic acid which acts on the copper.

Ferric acetate, $Fe_2(C_2H_3O_2)_6$, is used in medicine, and an insoluble oxy-acetate is often obtained in the course of analyses of minerals containing iron.

Ferrous acetate, $Fe(C_2H_3O_2)_2$. An impure form is obtained by dissolving iron in crude acetic acid. It is used in dyeing.

Aluminum acetate, $Al_2(C_2H_3O_2)_6$, is used in dyeing and calico printing.

Propionic (Tritylic) Acid, $HC_3H_5O_2$, is of comparatively little importance.

Butyric (Tetrylic) Acid, $HC_4H_7O_2$. This may be obtained from butter fat, and from some fruit flavors, and also by fermentation of sugar with cheese and chalk. Two isomeric modifications are known, called respectively normal (or a) butyric, and iso- (or β) butyric. Both are colorless liquids, having the disagreeable odor of rancid butter.

Valeric (Pentylic) Acid, $HC_5H_9O_2$, is found in valerian root and in other plants. Four isomeric modifications are possible, of which three are known. They have different specific gravities and boiling points. The ordinary form, a valeric acid, is a colorless liquid of a very disagreeable odor. Several valerates, often called valerianates, are used in medicine; among these are those of zinc and ammonium.

Caproic (Hexylic) Acid, $HC_6H_{11}O_2$, is a clear, oily liquid, of disagreeable odor; it may be obtained from butter fat.

Palmitic Acid may be obtained from many of the natural solid animal fats, also by saponifying palm oil. It is a solid, fat-like body, insoluble in water.

Margaric Acid. A mixture of stearic and palmitic acids was long mistaken for this acid. The real acid is now known, but has no special interest.

Stearic Acid can be obtained from most of the solid animal fats, and in some vegetable fats. It is a white, crystalline body which can be distilled. It is insoluble in water. Among other uses for it is the manufacture of candles. The white candles called stearine are generally made of stearic acid.

Salts of the Higher Fat Acids. By substituting the single atom of replaceable hydrogen of the fat acids we obtain a series of bodies which might be called "soaps," although it is only with the higher members of the series that the peculiar physical and chemical characters of the soaps

are seen.   Odling has pointed out, however, that even sodium acetate will form a slight lather with water.   The derivatives of the lower members are generally soluble in water, but in the higher members most of the compounds are insoluble, except those formed by potassium, sodium and ammonium.   With lead, calcium and zinc, for instance, we get insoluble soaps.   The chemistry of soap is explained elsewhere.

ETHERS OF THE FAT-ACIDS.

The monad alcohol radicles give with these acids compounds which are more or less volatile and odorous.   They are known as compound *ethers* or *esters*, and some of them are identical in composition, some only in odor, with fruit and flower essences, and based on this has sprung up an extensive business of preparing artificially these flavors.   The general method of preparation is to heat a mixture of the sodium salt of the proper acid and the alcohol containing the proper radicle with sulphuric acid. Thus, to produce ethyl acetate we would heat sodium acetate, ethyl alcohol and sulphuric acid.

$$C_2H_5HO + NaC_2H_3O_2 + H_2SO_4 = C_2H_5C_2H_3O_2 + NaHSO_4 + H_2O.$$
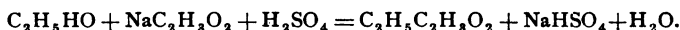
By using pentyl alcohol and sodium valerate, pentyl valerate would be formed, and so on.   Amyl acetate constitutes a banana essence; amyl valerate is apple essence, amyl butyrate has the odor of pine-apples.   By various mixture of these and other ethers almost any flavor may be imitated.

SUBSTITUTION DERIVATIVES.

The hydrogen that is part of the radicle of these acids may be substituted by members of the chlorine group, particularly by chlorine itself.   From acetic we get three compounds, all of which closely resemble the original acid.

$HC_2H_3O_2$............................. Acetic acid.
$HC_2H_2ClO_2$........................... Monochlor-acetic acid.
$HC_2HCl_2O_2$........................... Di   "   "   "
$HCCl_3O_2$ .... Tri   "   "   "

The last has recently been introduced as a test, by coagulation, for albumin in urine.   These substitution compounds, obtained by direct action, must be distinguished from those produced by the action of phosphorous chloride, PCl_3, on the strong acids, by which a molecule, HO, hydroxyl, is removed and an atom of chlorine substituted.   These bodies are called *acid chlorides*, and are named by attaching the syllable "yl" to the name of *the acid;* from acetic acid, for instance, we get *acetyl chloride*, C_2H_3OCl. *The acid chlorides* thus formed are of interest because from them the *anhy-*

drides can be formed by heating the acid chloride with a salt of the original acid, while by using the salt of some other acid a *mixed anhydride* can be formed. Thus:—

<table>
<tr><td>Potassium
acetate.</td><td>Acetyl
chloride.</td><td></td><td>Acetic
anhydride.</td></tr>
</table>

$$KC_2H_3O_2 + C_2H_3OCl = KCl + (C_2H_3O)_2O.$$

<table>
<tr><td>Potassium
formate.</td><td>Acetyl
chloride.</td><td>Formic-acetic
anhydride.</td></tr>
</table>

$$KCHO_2 + C_2H_3OCl = KCl + (CHO)(C_2H_3O)O.$$
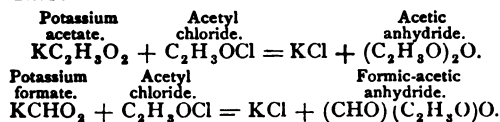
OLEFINS, OR METHENE SERIES.

The second member of this series, ethene, C_2H_4, was called, when first discovered, olefiant (oil-making) gas, because it combines with chlorine to form an oily liquid; for this reason the series has been called the *olefins*. They are dyad radicles, which form alcohols, ethers and other derivatives; but these derivatives are greater in number than from monad radicles, on account of the higher atomicity. Thus two series of acids are yielded by the action of oxygen on the alcohol, instead of one, as in the case of the monad radicles. The hydrocarbons themselves, with one or two exceptions, are not of much interest; the first member has not yet been obtained and is omitted from the list. Breaks also occur after the tenth member.

Name.	Melting Point.		Boiling Point.	
	F.	C.	F.	C.
Ethene............	.....	.....	.....	.....
Tritene	.....	.....	0.4	—18
Tetrene	.....	.....	33.8	1
Pentene...........................	.....	.....	95	35
Hexene...................	.....	.....	149	65
Heptene...................	.....	.....	205	96
Octene	.....	.....	248	120
Nonene	.....	.....	284	140
Decene...........................	.....	.....	320	160
Pentedecene	.....	.....	482	250
Hexdecene	.....	.....	527	275
$C_{20}H_{40}$............................	.....	.....	752	400
$C_{27}H_{54}$............................	135	57	.....	.....
$C_{30}H_{60}$............................	144	62	.....	.....

It will be seen that the ratio between the weights of the hydrogen and carbon is the same in each member of the series. Thus, if we take, for example, ethene, pentene and hexdecene, we have the following ratios:—

<table>
<tr><td>Ethene.</td><td>Pentene.</td><td>Hexdecene.</td></tr>
<tr><td>$C_2 = 24$</td><td>$C_5 = 60$</td><td>$C_{16} = 192$</td></tr>
<tr><td>$H_4 = 4$</td><td>$H_{10} = 10$</td><td>$H_{32} = 32$</td></tr>
</table>
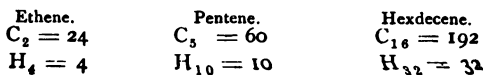
In each case the ratio is six parts of carbon to one part of hydrogen, so that the percentage composition is the same throughout the series, but the molecular weight increases. The members of the series are polymeric isomers. The methods of preparation of the olefins are not important. One of the simplest is by the action of dehydrating agents, sulphuric acid, phosphoric anhydride, on the alcohols of the monad radicles. Thus, with common alcohol:—

$$C_2H_5HO + H_2SO_4 = C_2H_4 + H_2O + H_2SO_4.$$
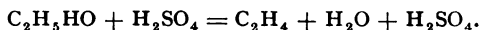
DERIVATIVES FROM THE OLEFINS.

The olefins combine directly with the chlorine group to form dichlorides. Ethene dichloride, $C_2H_4Cl_2$, was originally called *Dutch liquid*, because discovered by an association of Dutch chemists.

By indirect means oxides and ethers may be formed, and also hydroxides, containing, of course, two molecules of HO and known as DIATOMIC ALCOHOLS or GLYCOLS. Each of these alcohols yields by oxidation *two* acids, one derived by the replacement of two atoms of hydrogen by one atom of oxygen, and the other by the replacement of four atoms of hydrogen by two atoms of oyxgen. The first is the *lactic acid* series; the second, the *oxalic acid* series. For instance, ethene glycol gives the following:—

$$C_2H_4(HO)_2 + O_2 = H_2O + \overset{\text{Glycolic acid.}}{HC_2H_3O_3}.$$

$$C_2H_4(HO)_2 + O_4 = H_2O + \overset{\text{Oxalic acid.}}{H_2C_2O_4}.$$
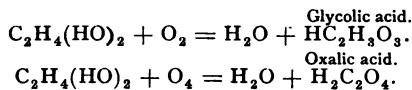
The following table shows some of the known derivatives of the olefins:—

Radicle.	Oxides, ethers.	Hydroxide alcohols.	Acids by first oxidation.	Acids by second oxidation.
C_2H_4	C_2H_4O	$C_2H_4(HO)_2$	Glycolic acid. $HC_2H_3O_3$	Oxalic acid. $H_2C_2O_4$
C_3H_6	C_3H_6O	$C_3H_6(HO)_2$	Lactic acid. $HC_3H_5O_3$	Malonic acid. $H_2C_3H_2O_4$
C_4H_8	C_4H_8O	$C_4H_8(HO)_2$	Oxybutyric. $HC_4H_7O_3$	Succinic. $H_2C_4H_4O_4$

Several higher members of each of these series are known; carbonic acid may be regarded as the first member of the first series, and therefore as a derivative of methene glycol, $CH_2(HO)_2$, which, however, has not been obtained.

Ethene oxide, C_2H_4O, is isomeric with common aldehyde, but is not *identical with it.*

Acid Derivatives of the Glycols. These are the most important. The first (lactic) series is monobasic, that is, has a single atom of replaceable hydrogen, except carbonic acid which has two; the second (oxalic series) is dibasic, that is, has two atoms of replaceable hydrogen.

LACTIC SERIES.

Name.	Formula.	Melt. Pt. F	Melt. Pt. C.	Boiling Pt. F	Boiling Pt. C.	Source.
Glycolic....	$HC_2H_3O_3$	176	80	212	100	By oxidation of ethene glycol.
Lactic......	$HC_3H_5O_3$					By fermentation of milk sugar.
Oxybutyric	$HC_4H_7O_3$					By oxidation of butyric acid.
Oxyvaleric	$HC_5H_9O_3$	76	80			By oxidation of valeric acid.
Leucic......	$HC_6H_{11}O_3$	164	73	212	100	Occurs in animal products also formed by decomposition of horn glue, etc.

OXALIC SERIES.

Name.	Formula.	Melt. Pt. F	Melt. Pt. C.	Source.
Oxalic........	$H_2C_2O_4$			Oxidation of sugar, starch and cellulin.
Malonic......	$H_2C_3H_2O_4$	284	140	Oxidation of malic.
Succinic	$H_2C_4H_4O_4$	356	180	Distillation of amber; oxidation of fat-acids.
Pyrotartaric.	$H_2C_5H_6O_4$	234	12	Action of heat on tartaric acid.
Adipic.......	$H_2C_6H_8O_4$	284	140	" " nitric on sebacic acid.
Pimelic......	$H_2C_7H_{10}O_4$	273	134	" " potassium hydroxide on camphoric acid.
Suberic......	$H_2C_8H_{12}O_4$	257	25	Action of nitric acid on cork or castor oil.
Anchoic.....	$H_2C_9H_{14}O_4$	241	16	Action of nitric acid on coco-nut oil.
Sebacic......	$H_2C_{10}H_{16}O_4$	261	127	Distillation of oleic acid.
Rocellic	$H_2C_{17}H_{30}O_4$	270	32	Exists in some lichens.

Glycolic acid, $HC_2H_3O_3$, is a white crystalline solid, soluble in water, alcohol and ether.

Lactic acid, $HC_3H_5O_3$. This important acid exists in at least three isomeric modifications.

(*a*) *Ordinary lactic acid* exists in gastric juice, in Turkey opium, and is a product of fermentation, especially of milk. It is a colorless, syrupy, very sour liquid, which has not yet been obtained in the solid state. It can be obtained in quantity by allowing a mixture of cane sugar, cheese, sour milk and chalk, or zinc oxide, to ferment for several days. The resulting calcium or zinc lactate can be purified and the lactic acid obtained from it.

(*b*) Paralactic acid and (*c*) ethene-lactic acid, two isomers of ordinary lactic acid, occur together in muscular tissue, and were formerly included under the title sarcolactic acid.

Several lactates are used in medicine.

Leucic acid, $HC_6H_{11}O_3$, is formed during putrefaction, and by boiling horn with dilute sulphuric acid, and is also found in the animal organism. Leucic acid crystallizes in needles, forms white, shining scales, and is slightly soluble in water.

Oxalic acid, $H_2C_2O_4$. The free acid and its salts, especially acid potassium oxalate, occurs in many plants, generally in the form of crystals —called raphides—deposited in special cells in the leaves or stems. Calcium oxalate is an occasional ingredient of urinary calculi. The acid may be made either by the oxidation of sugar by strong nitric acid, or by the action of caustic alkali on sawdust. The latter process is now generally used. The reactions are complicated. Sodium oxalate is produced by the reaction of sodium on carbon dioxide. This process, although of no practical value, is an interesting example of organic synthesis.

$$Na_2 + 2CO_2 = Na_2C_2O_4.$$
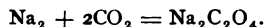
Oxalic acid forms colorless crystals, having the formula $H_2C_2O_4 + 2H_2O$. The two molecules of water are driven out at 212° F. (100° C.), and at a higher temperature the acid volatilizes. It is freely soluble in water, and is one of the most rapidly fatal poisons known. Death has occurred in ten minutes after administration. The antidote is lime. Preparations of the acid are sold under the misleading names of salt of sorrel and salt of lemon, and used for taking out ink stains. Oxalic acid, treated with strong sulphuric acid, breaks up thus :—

$$H_2C_2O_4 = H_2O + CO_2 + CO.$$
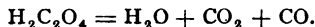
When distilled in contact with glycerine, it produces formic acid and carbon dioxide.

$$H_2C_2O_4 = CO_2 + HCHO_2.$$

Ammonium oxalate, $(NH_4)_2C_2O_4$, form white crystals, soluble in water, and much used as a test for calcium.

Calcium oxalate, CaC_2O_4, is thrown down as a white precipitate by adding an oxalate to calcium chloride. In this form it is not markedly crystalline, but it is sometimes found in the urine in microscopic octahedral or dumb-bell crystals. In larger masses it constitutes mulberry calculus.

Malonic acid, $H_2C_3H_2O_4$, is not important. It is formed by the oxidation of malic acid.

Succinic acid, $H_2C_4H_4O_4$. This occurs in amber and other resins; also in small quantities in some animals. It can be produced by many methods. It is one of the products of the action of nitric acid on organic bodies. All the higher fatty acids produce it when thus oxidized. It is also produced in fermentation. It forms colorless crystals, soluble in water. There is an isomeric modification, iso-succinic acid.

The other acids of this series are sufficiently described in the table.

Somewhat related to the series just described, although not necessarily referable to the same radicles, are two important vegetable acids, malic and tartaric. The relation is especially with succinic acid, from which they differ only in amount of oxygen.

$$\text{Succinic} \dots\dots\dots\dots\dots\dots\dots\dots\dots H_2C_4H_4O_4.$$
$$\text{Malic} \dots\dots\dots\dots\dots\dots\dots\dots\dots H_2C_4H_4O_5.$$
$$\text{Tartaric} \dots\dots\dots\dots\dots\dots\dots\dots\dots H_2C_4H_4O_6.$$

Malic acid, $H_2C_4H_4O_5$, occurs in many sour fruits, as apples, pears and mountain ash berries. It may be made artificially from succinic acid. It is crystalline, sour, soluble in water and alcohol. The malates are mostly soluble in water. Sweet cherries contain potassium malate.

Tartaric acid, $H_2C_4H_4O_6$, is found in many plants, but especially in grapes, where it exists as acid potasssium tartrate, $KHC_4H_4O_6$. This is somewhat soluble in water, but scarcely soluble in dilute alcohol; and hence, in the manufacture of wine, as the fermentation advances, the quantity of alcohol increases, and the tartrate deposits as a red mass called *argols* or *tartar*; this is dissolved in water and purified by crystallization; it is *cream of tartar* (called very wrongly by some writers cremor tartar). Tartaric acid presents several isomeric modifications, which remind us somewhat of the different forms of glucose. The common form, as obtained from wine, usually rotates the ray of polarized light to the right. Another form is sometimes found in tartar, which has no effect on polarized light, but may be decomposed into two acids having opposite effects. The inactive form is called *racemic* acid; two active forms are called respect-

D

ively dextro- and lævo-tartaric acid. The important tartrates are those derived from the common form. The acid itself is a crystalline body, soluble in water, and forming a very sour solution which develops a fungous growth and decomposes.

Acid potassium tartrate is a white crystalline body, very sour, and not very soluble in cold water. It is used in effervescing powders.

Potassium tartrate, $K_2C_4H_4O_6$, is called soluble tartar.

Sodio-potassium tartrate, $NaKC_4H_4O_6$, is known as *Rochelle salt*.

Tartar emetic is made by boiling acid potassium tartrate with oxide of antimony, by which an atom of hydrogen is replaced by the molecule SbO. The formula for tartar emetic is, $K(SbO)C_4H_4O_6$.

Citric acid, $H_3C_6H_5O_7$, is the acid of lemons and oranges, and is also found in some other fruits. It is a crystalline body, very sour, and easily soluble in water. It is used in the preparation of effervescing mixtures, but some of the so-called effervescing citrates contain tartaric instead of citric acid.

METHENYL SERIES.

These are triad radicles of the general formula C_nH_{2n-1}. The first member, CH, methenyl, may be regarded as existing in chloroform. The most important member of the group is tritenyl, C_3H_5, also called propenyl. The hydroxide of the radicle, consisting of three molecules of hydroxyl, since the radicle is a triad, is glycerin, $C_3H_5(HO)_3$. Many of the common oils and fats are compound ethers of tritenyl, and when these bodies are treated with alkaline solutions, such as caustic soda, the compound ether is broken up, a new salt and tritenyl hydroxide is formed. Thus, one of the important ingredients of common animal fat is tritenyl stearate, and with caustic soda—common lye—the action would be :—

$$\underset{\text{Sodium Stearate.}}{} \quad \underset{\text{Glycerin.}}{}$$
$$(C_3H_5)(C_{18}H_{35}O_2)_3 + 3NaHO = 3NaC_{18}H_{35}O_2 + C_3H_5(HO)_3.$$
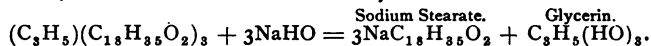
Sodium stearate is a *soap*, and the above process is called saponification. The formation of glycerin can also be brought about by the use of super-heated steam. This method is the one now generally used in manufacturing operations, since it gives the fat-acids in the free condition, thus :—

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3H_2O = C_3H_5(HO)_3 + 3HC_{18}H_{35}O_2.$$
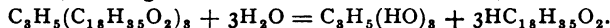
Glycerin. $C_3H_5(HO)_3$. As obtained by the processes just given, glycerin is mixed with various impurities. The pure substance is a colorless, viscid liquid, miscible in all proportions with water and alcohol. Specific gravity 1.27. It has a marked sweet taste, absorbs water from the air, but does not otherwise change. It has been used on this account as a *substitute for water* and alcohol in gas regulators and meters, and similar

machinery. It cannot be distilled without decomposition, except under low pressure. It solidifies at about — 40° F. and C. It dissolves a great many substances, standing, in fact, next to water in its range of solvent powers. It is produced in small quantity during the fermentation of sugar, hence is often found in ordinary liquors. It is sometimes called the " sweet principle of fats," but it is obvious, from the above reactions, that it does not exist in fats, and possesses no chemical analogy to them. It is an alcohol, and is probably somewhat analogous to the sugars. Its use, therefore, as an application to the skin as a substitute for the emollient oils has no chemical justification.

When treated with strong nitric acid, it forms a tri-nitro-derivative known as nitro-glycerin or glonoin, $C_3H_5(NO_8)_8$, which may be regarded as tritenyl nitrate. This is powerfully explosive, especially by percussion. It is now extensively used as a blasting agent, being generally mixed with some inert powder, such as fine silica. This makes it more safe to handle. Such a mixture constitutes dynamite.

FATS AND FIXED OILS.

The fats and fixed oils are almost all compound ethers of tritenyl. Most of the natural forms are mixtures of two or more distinct ethers. Names are applied to them according to the acid from which the ether was derived. Thus, tritenyl stearate, $C_3H_5(C_{18}H_{35}O_2)_8$, is called *stearin ;* tritenyl butyrate, $C_3H_5(C_4H_7O_2)_8$, is called *butyrin*, and so on. These substances, therefore, constitute the *proximate principles*. The fixed oils are fats with a low melting point, and may be divided into two classes: drying-oils, which absorb oxygen from the air, and become hard and resinous, such as linseed and poppy oil; non-drying oils, which remain fluid, as castor and sperm oil. Many fats and oils undergo partial decomposition in the air, producing a free acid ; this is called rancidity. As already mentioned, when caustic alkali is added to a fat, decomposition takes place, a salt is formed constituting a soap, and glycerin is produced. The principle of the reaction is given in connection with the description of glycerin. Soaps produced by potassa are usually soft; those from soda, hard ; those made from other oxides are mostly insoluble in water. This latter fact explains the curdling action of limestone waters. The calcium and magnesium compounds in these waters produce insoluble soaps. When soaps of the alkali metals are treated with cold water they decompose into acid salt, which precipates and makes the soap-suds, and a small amount of alkali, which dissolves and gives the cleansing action.

A decomposition of the fats may be produced by the action of super-

heated steam. The fat-acids may also be obtained by adding a strong acid to ordinary soaps.

The fats existing in warm-blooded animals are generally solid at ordinary temperatures; those existing in cold-blooded animals are generally liquid. They are all insoluble in water, but are soluble in boiling alcohol, and in ether, chloroform, benzene and carbon disulphide at all temperatures. They are decomposed by heat, and consequently cannot, under ordinary circumstances, be distilled.

The following table shows the names and properties of the important fats.

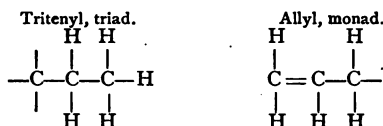| Name.	Sp. Gr.	Melting Point. F.	C.	
Linseed......	0.939	—13	—25	Contains linolein.
Walnut......	0.925	0	—18	
Hemp........	0.928	—13	—25	
Poppy........	0.925	0	—18	
Croton........	0.943			" tiglin, crotonin and valerin.
Castor........	0.969	—14	—26	" ricinolein.
Olive.........	0.918	32	0	Olein, palmitin, and perhaps stearin.
Almond......	0.918	—13	—25	Almost entirely of olein.
Sesamé......	0.925			
Rape.........	0.916	21	—6	Brassin and olein.
Mustard......	0.916	0	—18	Erucin.
Colza.........	0.913			
Cotton........	0.928	32	0	
Sunflower...		5	—15	
Human......				Olein and margarin.
Sperm........	0.868	45	7	
Whale.......	0.927	32	0	
Cod-liver....	0.927	30	—1	
Tallow	0.929	104	40	Stearin, palmitin and olein.
Lard (solid)	0.932	90	32	" " " "
Lard (oil)...	0.915	32	0	Olein.
Butter........	0.939	82	28	Contains numerous fats, principally olein, palmitin and butyrin.
Palm.........	0.860	81	27	Palmitin and olein.
Nutmeg......		87	31	
Coco	0.870	68	20	Laurin, myristin, palmitin and stearin.
Cacao........	0.948	85	30	
Laurel.......				Laurin.
Wax	0.96	145	63	Melissyl palmitate and cerotic acid.
Spermaceti..	0.940	120	49	Cetyl palmitate.

The proximate constituents of the common fats are given under condensed names, the signification of which is as follows :—

> Stearin is tritenyl stearate.
> Palmitin is " palmitate.
> Margarin is " margarate.
> Butyrin is " butyrate.
> Olein is " oleate.

Oleic acid is not a member of the same series with the other acids. It belongs to a series beginning with acrylic acid, $HC_8H_3O_2$, and is elsewhere described.

ALLYL AND DERIVATIVES.

Allyl, C_3H_5, is isomeric with tritenyl, but unlike it is a monad, the carbon atoms neutralizing the valency of each other more completely than in the case of tritenyl. By graphic formula the difference may be thus represented :—

Tritenyl, triad.

$$
\begin{array}{ccc}
 & H & H \\
 & | & | & | \\
-C & -C & -C & -H \\
 & | & | & | \\
 & H & H
\end{array}
$$

Allyl, monad.

$$
\begin{array}{ccc}
H & & H \\
| & & | \\
C & = C & -C & - \\
| & | & | \\
H & H & H
\end{array}
$$

Allyl alcohol is C_3H_5HO. Allyl is chiefly interesting on account of the occurrence in nature of two of its compounds, allyl sulphide, $(C_3H_5)_2S$, which is the essential oil of garlic, and allyl sulphocyanide, C_3H_5CNS, volatile oil of mustard. Allyl aldehyde, C_3H_4O, is one of the products of the decomposition of fats by heat, and is the main cause of the irritating vapors which are caused by such decomposition. The oxidation of allyl aldehyde gives acylic acid, which is the first member of the long series of acids existing in some of the fats. The most important of this list is oleic acid.

Oleic acid, $HC_{18}H_{33}O_2$, exists in most natural fats and non-drying oils as olein—tritenyl oleate. It is solid at 57° F. (14° C.). Above this temperature it is a clear liquid, lighter than water, and insoluble in it, but soluble in alcohol and ether. Crude oleic acid, made by the decomposition of fats by steam, as mentioned elsewhere, is used in soap-making, under the name of red oil. Various oleates, *e. g.*, copper, bismuth, zinc and mercury oleates, are now used as substitutes for ointments. They are usually prepared by the reaction of sodium oleate with some suitable compound. Thus copper oleate is formed by mixing copper sulphate with sodium oleate.

TURPENES.

The series beginning with tritone, C_3H_2, is but imperfectly known. The eighth member, $C_{10}H_{16}$, has great interest because a large number of *volatile* or *essential oils* have this composition. These oils often exist in plants, in association with oxidized products of higher boiling point, called resins. This mixture constitutes oleo-resin. When this is heated the oil distills and the resin is left. Gum is also sometimes present, thus making a *gum-resin*. A *balsam* is a similar mixture containing benzoic or cinnamic acid. Of the volatile oils having the composition, $C_{10}H_{16}$, the most important is:—

Oil of Turpentine, obtained from turpentine, which is an exudation from pine trees, and consisting of resin and volatile oil. On being distilled the volatile oil is collected in a receiver; the resin remaining constitutes common rosin. Oil, or spirits of turpentine, is a thin, colorless liquid. It is lighter than water, boils at 320° F. (160° C.), and is a valuable solvent. It is partially oxidized in the air. Some of the oils which have the same composition as oil of turpentine are lemon, bergamot, coriander, hop, juniper and valerian. They are called *essential oils*, are mostly lighter than water, and freely soluble in ether and alcohol. Though agreeing in composition, they differ in specific gravity, boiling point and effect on polarized light. The cause of this difference in properties is not understood. Many of these oils, by exposure to the air, undergo oxidation and other changes, and in time become resinous and acquire an odor something like the oil of turpentine.

Many of the essential oils can be separated, by cooling, into solid and liquid portions, called, respectively, the stearoptene and the elæoptene.

CAMPHORS AND RESINS.

Plants furnish us with a number of oxidized turpenes, among which are the *camphors* and *resins*.

Common camphor, $C_{10}H_{16}O$, obtained from the camphor laurel, is a white, crystalline solid, volatile at ordinary temperatures. It is slightly soluble in water, and freely in alcohol and ether. A small lump of camphor placed in water moves about for some time actively, but a minute quantity of grease will at once stop the motion. By the action of hydrochloric acid on oil of turpentine a body having the odor of camphor is formed.

Another form of camphor, called Borneo camphor, has the formula, $C_{10}H_{18}O_2$.

*Resins* include a large group, of which many are true acids, and form salts, constituting resin soaps.

Common rosin is the residue from the preparation of oil of turpentine. It is a mixture of two acids. As a class the resins are easily fusible, but not volatile, insoluble in water but soluble in alcohol.

Amber and copal are fossil resins—that is, are found in fossil vegetable matter. Lac, mastic, sandarach and dragon blood are used in varnishes.

Caoutchouc and *gutta percha* are turpenes found in the juice of plants. They are insoluble in water, but in the plant are usually in suspension, very finely divided so as to make a milky liquid, called an emulsion. Caoutchouc is elastic; gutta percha is not. Both are capable of combining with sulphur when heated to about 300° F. (150° C.). The process is called vulcanizing, and the hardness of the product can be regulated by the amount of sulphur and the temperature used, so that valuable materials are prepared in this way. Caoutchouc dissolves in benzene and petroleum spirit; a solution of it mixed with a little lac is marine glue. Gutta percha is soluble in chloroform; the solution constitutes *liquor gutta perchæ.*

BENZENES.

Benzene, C_6H_6, phenyl hydride, sometimes called benzol, is the first member of a series which possesses great interest on account of the number of isomeric compounds which have been obtained. The hydrogen is susceptible of replacement by various elements and radicles, and not only may we get, in this way, a number of compounds, but it appears that different atoms of H, replaced by the same substance, give different bodies. Thus, dibromo-benzene, $C_6H_4Br_2$, exists in three different forms. Such facts are generally explained by graphic formula, in which the substituting bodies are shown in different positions in different isomers. We may represent benzene and its three dibromide compounds:—

Benzene.   Ortho dibromo-benzene.
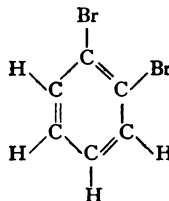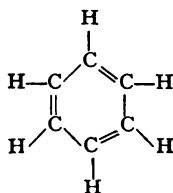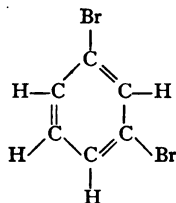
Meta dibromo-
benzene.
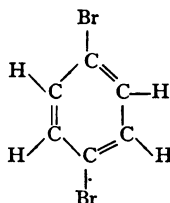
Para dibromo-
benzene.

In such formulæ it is usual in order to prevent confusion, to write the carbon molecule and to omit the hydrogen. The three dibromo-benzene, given above, would, for instance, be written more compactly:—
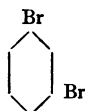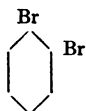
For the same reason the terms, ortho, meta, and para may be abbreviated to *o*, *m* and *p*.

In addition to the substitution compounds the benzenes are capable of acting as hexad molecules by, as we may suppose, the unlinking of some of the bonds between the carbons. We might represent the difference, graphically, thus :—

Benzene
saturated molecule.

Benzene
hexad molecule.
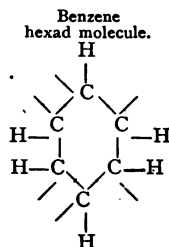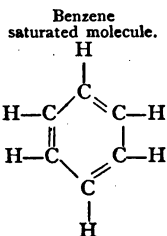
These additive compounds are, of course, different from the substitutive compounds, and are much less stable. Vast numbers of benzene derivatives *have been described.* The following is

THE BENZENE SERIES.

Name.	Formula.	
Benzene....	C_6H_6	Two isomeric forms are included under this name.
Toluene....	C_7H_8	
Xylene	C_8H_{10}	Four " " " " " " "
Cumene....	C_9H_{12}	Five " " " " " " "
Cymene....	$C_{10}H_{14}$	Six " " " " " " "
	$C_{11}H_{16}$	Three isomeric bodies of this composition are
	$C_{12}H_{18}$	known.
	$C_{13}H_{20}$	

Benzene, C_6H_6, sometimes called *Benzole,* may be made in several ways, among which are the distillation of a mixture of benzoic acid and slaked lime, and the destructive distillation of coal. The latter process is the one from which most of the benzene of commerce is now derived. In the manufacture of illuminating gas from coal a quantity of tar is produced, and from this, by fractional distillation, the benzene is obtained. When pure, it is colorless, mobile, boiling at 81° C. (177° F.), and solidifying at 0° C. (32° F.). It is lighter than water, and insoluble in it; mixes with alcohol and ether, and is very inflammable. It is largely used as a solvent for resins and fats, especially in organic analysis. When treated with strong nitric acid it yields nitro-benzene.

$$C_6H_6 + HNO_3 = C_6H_5(NO_2) + H_2O.$$

Nitro-benzene is a yellow liquid, having an odor which resembles somewhat that of bitter almond oil. It is now used as a cheap perfume, especially in soaps, under the name of *oil of myrbane.* It is distinctly poisonous, producing, even in small doses, unconsciousness, with marked delay in respiration. Its use in soap cannot, however, be regarded a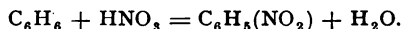s seriously objectionable. When nitro-benzene is heated with nascent hydrogen it is converted into *aniline,* $C_6H_5H_2N$. By distilling nitro-benzene with potassium hydroxide, azo-benzene, $(C_6H_5)_2N_2$, is obtained.

Toluene, C_7H_8, is a limpid liquid, lighter than water, boiling at 230° F. (110° C.), and not solidifying at the freezing point of water. It generally exists in crude benzene.

Starting with benzene, we have a series of hydrocarbons, differing by the unusual ratio, C_4H_2. Thus,

C_6H_6, benzene. $C_{14}H_{10}$, anthracene.

$C_{10}H_8$, naphthalene. $C_{18}H_{12}$, chrysene.

These bodies, all existing in the destructive distillation of coal, have the common property that, under the influence of oxidizing agents, two atoms

of hydrogen can be replaced by *two* atoms of oxygen. The body so produced is called a quinone, and by the action of nascent hydrogen they furnish a hydroquinone. The character of these changes is shown by the following formulæ :—

Benzene.	Quinone.	Hydro-quinone.
C_6H_6	$C_6H_4O_2$	$C_6H_4(HO)_2$
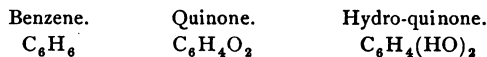
Each one of the four hydrocarbons given above is the member of a homologous series, but it will not be necessary to describe all these.

Naphthalene, $C_{10}H_8$, is obtained, by redistilling coal tar, in the form of white, somewhat fragrant, crystalline scales. It melts at 176° F. (80° C.). It is slightly soluble in boiling water. When dissolved in hot, strong sulphuric acid, two isomeric *naphthalene-sulphuric acids* are formed. From each of these, by the action of potassium hydroxide, a body having the composition, $C_{10}H_7HO$, naphthyl hydroxide, is formed. These bodies are generally known respectively as a and β naphthol. β naphthol is now much used in the treatment of diseases of the skin.

By the action of oxidizing agents naphthalene is converted into phthalic acid, $H_2C_6H_4O_4$. If this be converted into calcium phthalate, $CaC_6H_4O_4$, and heated with lime for several hours, calcium benzoate, $Ca(C_7H_5O_2)_2$, is formed. These reactions form an important source for benzoic acid.

Anthracene, $C_{14}H_{10}$. This is obtained from coal tar, being one of the least volatile ingredients. The crude article is a solid, generally of a greenish-yellow color, and a peculiar odor which is not unlike that of a decayed tooth. The pure anthracene is crystalline, and gives a fine blue fluorescence. It melts at 213° C. (415° F.). It is insoluble in water. Its oxidation products are of great importance because from them may be obtained *alizarine*, a body to which the valuable dye madder owes its color. The artificial production of the madder color has been extensively carried on of late years. The outline of the process is given on a former page, as an illustration of organic synthesis.

PHENYL SERIES.

Phenyl, C_6H_5, is a monad radicle, existing in a number of coal tar products. Its hydroxide, C_6H_5HO, is commonly known as carbolic, phenic or phenylic acid. It is hardly a true acid, but is so called from a power of taking up bases and forming bodies like salts, which are generally called phenates. It is preferably called *phenol* or *phenylic alcohol*.

Phenol exists in coal tar, and can also be made artificially by several processes. It forms colorless crystals, is very deliquescent and soluble in

water, melting at 93° F. (34° C.), and boiling at 370° F. (187° C.). It has a peculiar odor, much like that of kreasote, which is a somewhat similar body, obtained from wood tar. Pure phenol remains unaltered in the air, but the commercial article generally acquires in time a pink tinge. By the action of nitric acid on phenol the complete result is

Picric acid, or trinitro-phenol, $C_6H_3(NO_2)_3O$, a deep yellow crystalline substance, very soluble in water. It is also obtained when nitric acid acts upon many other substances, as indigo, silk, wool, etc. In the arts it is employed as a dye for silk and wool. It is monobasic, and some of its salts are explosive. Its solution possesses the power of coagulating albumin, and is much used as a test for that substance.

Phenylamine, $C_6H_5H_2N$, is elsewhere described under the name of aniline.

Cresol, C_7H_7HO, cresylic acid. This body bears the same relation to toluene, C_7H_8, that phenol does to benzene. Phenol is an oxybenzene; cresol is an oxy-toluene, and may be regarded as the hydroxide of a radicle, cresyl. It exists in coal tar, and, when pure, crystallizes in white needles, which melt at 36° C. (95° F.). It is often present in commercial phenol.

Kreasote, which is obtained from wood tar, is a mixture of various bodies. Commercial kreasote is often largely phenol.

Orcin, $C_7H_8O_2$, is a product having some of the qualities of an acid, derived from plants known as *lichens*. By oxidation it forms a bright red compound, which is used in dyeing. From the same lichens which yield orcin we can, by maceration with water, and allowing to ferment, obtain a red coloring matter, sparingly soluble in water, and instantly turning blue when neutralized with alkalies. This substance is *litmus*, and is used as a test for the presence of acid and alkalies.

BENZYL COMPOUNDS.

Benzyl, C_7H_7, is isomeric with the radicle of cresol and, of course, forms a hydroxide, C_7H_7HO, having the same formula as cresol. Benzyl hydroxide is a true alcohol, from which we may get by oxidation an aldehyde and an acid.

Benzyl aldehyde, C_7H_6O, is oil of bitter almonds. Its formation from amygdalin by a species of fermentation is pointed out elsewhere. It is a colorless liquid, heavier than water, and, as usually made, has the smell of hydrogen cyanide, since that body is formed from amygdalin at the same time as the oil. Oil of bitter almonds has been used in confectionery as a flavor. It is now largely substituted by nitro benzene.

Benzoic acid, $HC_7H_5O_2$, occurs in various resins, especially in *benzoin*. It is sometimes found in the urine of herbivora, and can be made artificially by several methods. One of these is given under naphthalene ; another is described under hippuric acid. Benzoic acid is a white crystalline solid, of pleasant odor, but very disagreeable taste. It dissolves but slightly in cold water, but more so in hot water and alcohol. It sublimes at a temperature below its boiling point.

Salicylic or **oxy-benzoic acid,** $HC_7H_5O_3$, differs, it will be seen, from benzoic acid only in having an additional atom of oxygen. It is, however, not made from benzoic acid, but from the action of carbon dioxide on a mixture of sodium phenate. The reaction is :—

<div align="center">Sodium phenate.   Sodium salicylate.</div>

$$NaC_6H_5O + CO_2 = NaC_7H_5O_3.$$
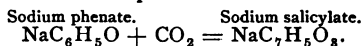
Sodium salicylate can also be obtained by the action of sodium hydroxide on salicin.

Salicylic acid forms prismatic crystals, which are sparingly soluble in water. The solution gives a deep violet color with ferric chloride.

Antiseptics. Many of the bodies which, enumerated above either as direct or indirect derivatives from benzene or its homologues, are now in extensive use as antiseptics. A distinguished English surgeon, Mr. Lister, has introduced their use into surgical operations, basing his views of their efficacy principally on the ground that the unfavorable results which often occur after such operations are due to the micro-organisms in the air. Phenol, salicylic acid, etc., destroy these micro-organisms, and are thus supposed to prevent their injurious action. Such methods constitute antiseptic surgery or Listerism. All surgeons have not agreed to the views of Mr. Lister, and it seems probable that a portion of the beneficial results which attend Mr. Lister's method are due to the enforced cleanliness which the method requires.

These bodies are undoubtedly preservative in character, and salicylic acid is especially used for preserving beer and the concentrated foods now so extensively sold. Its use, however, is objectionable.

SUGARS AND STARCHES.

Under this title is included a group of bodies exhibiting strong relationships, to each other, and features which distinguish them from most other organic bodies. Among the properties possessed by most of them is a power to affect a ray of polarized light, which is often so marked that it *may be utilized for detecting* and estimating the amount of the substance

present. A sweet taste, moderate deoxidizing power, partial inter-converti-bility and susceptibility to alcoholic fermentation, are also features which most of them possess. They all have nearly the same composition and contain only three elements, carbon, hydrogen and oxygen, the latter two always in the proportion in which they exist in water. The empirical formulæ of these have been accurately determined, but their rational formulæ are not definitely known. They have been regarded as alcohols or aldehydes containing complex radicles. They are commonly divided into three classes. In the following list the mark $+$ indicates that the substance rotates a ray of polarized light to the right; $-$ that it rotates to the left. Substances unmarked have no action:—

1. SUCROSES. (Sugars Proper) $C_{12}H_{22}O_{11}$	2. GLUCOSES. (Grape Sugars) $C_6H_{12}O_6$	3. AMYLOSES (Starch and Woody Fibre) $C_6H_{10}O_5$
Sucrose (Cane Sugar) $+$	Dextrose (Grape Sugar) $+$	Starch $+$
Lactose (Milk Sugar) $+$	Lævulose (Fruit Sugar) $-$	Dextrin $+$
Melitose $-$	Galactose $+$	Inulin
Melizitose $-$	Sorbite $+$	Gum
Trehalose $-$	Inosite.	Cellulin.

Sucrose, or **Cane Sugar**, $C_{12}H_{22}O_{11}$, exists in plants, especially sugar-cane and beet-root. It is extracted by pressure; the liquid is then treated with lime to neutralize free acid, boiled down carefully at a low temperature, the raw product decolorized by animal charcoal and finally crystallized. Sugar crystallizes in oblique prisms. Its properties are well known. When heated to 420° F. *caramel* is formed. By the action of dilute acids, or ferments, or even of heat alone, it is converted into a mixture of equal parts of glucose and lævulose, which mixture, on account of the greater effect of the lævulose on polarized light, rotates such rays to the left, and is therefore known as *inverted* sugar. Sugar, although freely soluble in water, is almost insoluble in alcohol and ether.

Lactose, or **Milk Sugar**. This has the same composition as cane sugar, but decidedly different properties. It exists in milk. It is much less sweet than cane sugar, and much less soluble in water. Milk sugar is much used as a diluting agent in homœopathic triturations.

The other members of the sucrose group are not important.

of gun-cotton and camphor is called *celluloid*. It is a tough, hard mass, which may be easily softened by heat, and then can be moulded into any shape. Mixed with zinc oxide it can be given the appearance resembling ivory; mixed with vermillion it is used as a substitute for vulcanized rubber in teeth-plates.

All the forms of cellulin yield nitro compounds analogous to gun-cotton.

Cellulin apparently exists in wood fibre in a state of combination, as it requires the action of strong chemical agents to produce the cellulin from the wood. Much remains, however, to be investigated in regard to this substance.

Glycogen. This is a white, amorphous powder, which gives a brown color with iodine, and by the action of ferments or dilute acids it will become dextrose (dextro-glucose). It therefore resembles starch, but is soluble in water. It is formed in the liver of several animals; also in yolk of egg and in some mollusca.

CHEMICAL RELATIONS OF SUGAR AND STARCH.

The sugars and starches are reducing agents, but not very energetic. The action is generally increased by the presence of strong alkalies. The tests for them are mostly dependent, upon their reducing action, upon the salts of copper, silver, bismuth and mercury. Glucose is the most active in this respect, and the other members of the class may generally easily be converted into glucose before being tested. The following are the best known tests:—

Moore's test depends on the fact that a solution of sugar becomes darker on being boiled with caustic alkali.

Trommer's test is performed by adding a few drops of copper sulphate, and a considerable amount of caustic soda or potassa. If sugar be present the application of heat will cause the precipitation of orange-red cuprous oxide, Cu_2O.

Boettger's test is performed in the same way, substituting bismuth oxy-nitrate for copper sulphate. A heavy black precipitate is formed.

The most accurate test is the production of alcohol and carbon dioxide by fermentation.

GLUCOSIDES.

Under this term is included a large number of bodies, mostly obtained from plants, and possessing the common quality of being easily susceptible of decomposition into several distinct substances, one of which is always glucose. They may be regarded as compound ethers, derived from glucose. They are sometimes quite complicated in composition, generally have marked medicinal qualities, and often, therefore, constitute the active principles of the plants from which they are obtained. Dilute acids and ferments are the usual means of producing the specific decomposition. Some of them, as they exist in plants, are associated with a body capable of acting as a ferment, and thus are decomposed as soon as exposed to heat and moisture, which causes the ferment to act.

Starch and most of the amyloses may be regarded as glucosides, since they yield glucose by the action of acids and ferments.

Amygdalin, $C_{20}H_{27}NO_{11}$, is spoken of in connection with the compounds of cyanogen. It exists in seeds of many plants of the order Rosaceæ, in association with a ferment called *synaptase* or *emulsion.* This acts immediately on the amygdalin, when the seeds are crushed in cold water; hence, in order to obtain the undecomposed glucoside, we must use boiling alcohol, which coagulates the synaptase and dissolves the amygdalin. It is a white, crystalline body, soluble in alcohol and water, but not in ether. The decomposition to which it is susceptible is shown in connection with the description of hydrogen cyanide.

SALICIN, $C_{13}H_{18}O_7$, is found principally in the bark and leaves of the *Poplar* and *Willow.* It crystallizes in white needles. Insoluble in ether, but soluble in water and alcohol. Salicin decomposes as follows:—

$$C_{13}H_{18}O_7 + H_2O = C_7H_8O_2 + C_6H_{12}O_6.$$
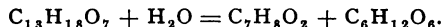
$C_7H_8O_2$ is called *saligenin.* Owing to the resemblance in taste and appearance between quinine and salicin, both being quite bitter, the latter is sometimes used as an adulterant of the former. The fraud may be detected by the addition of a drop of strong sulphuric acid, which gives no color with quinine, but produces a blood-red color with salicin.

Tannins. These are astringent principles, widely diffused in the vegetable kingdom. They dissolve in water and have an acid reaction; hence are often called tannic acid. They present numerous varieties, which possess the common property of forming insoluble compounds with gelatin, giving dark-colored precipitates with ferric salts. Their action on gelatin is taken advantage of in the preparation of leather, while by their action with ferric salts common ink is made.

E

Ordinary tannin, or gallo-tannic acid, occurs in nutgalls—excrescences formed on a species of oak by puncture by an insect—and sumach. It is usually seen as a loose, brittle, light-yellow, non-crystalline mass, very soluble in water and highly astringent. It gives a bluish-black precipitate with ferric salts. The common form is not entirely a true glucoside, but contains a large amount of digallic acid, $C_{14}H_{10}O_9$.

When tannin is boiled with dilute acids, or mixed with water and exposed to moist air, it forms gallic acid. The gallic acid may come either from the splitting up of the glucoside or the absorption of water by digallic acid. Thus:—

Tannin (glucoside).   Glucose.   Gallic acid.
$$C_{27}H_{22}O_{17} + 4H_2O = C_6H_{12}O_6 + 3C_7H_6O_5.$$
Digallic acid.   Gallic acid.
$$C_{14}H_{10}O_5 + H_2O = 2C_7H_6O_5.$$
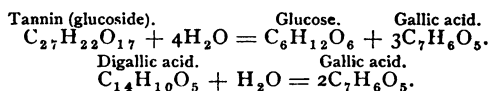
Gallic acid is elsewhere described.

The conversion of tannin into gallic acid is one of the sources of loss in the manufacture of leather, since gallic acid has no tanning qualities. The change can be prevented by antiseptic substances, such as sulphurous and boric acid, and solutions of these are now sold under the name of *anti-galline*. The process of tanning consists essentially in the tannin rendering the gelatinous matter of the hide insoluble, and therefore not liable to decomposition.

Solanin, $C_{43}H_{71}NO_{16}$, exists in plants of the order *solanacea ;* for instance in the young shoots of the potato.

MYRONIC ACID, $C_{10}H_{19}NS_2O_{10}$. This acid exists in the seed of the *Black Mustard*, as myronate of potassium, which is decomposed by an albuminous ferment contained in the mustard seed into allyl-sulphocyanate, glucose and acid potassium sulphate. Thus:—

$$KC_{10}H_{18}NS_2O_{10} = C_2H_5CNS + C_6H_{12}O_6 + KHSO_4.$$
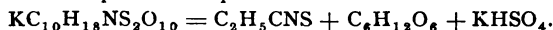
The allyl sulphocyanate is the substance which gives to mustard its medical virtue, and as hot water would coagulate the albuminous ferment, and thus prevent the reaction, mustard plaster must be made with cold water. White mustard seed contains a glucoside, *sinalbin.*

Indican, $C_{52}H_{62}N_2O_{34}$, occurs in several plants, especially known, botanically, as *indigofera.* It is a brown syrup which, by boiling with acid, yields the color known as *indigo blue* (indigotion), $C_{16}H_{10}N_2O_2$. Indigo blue is obtained from the plants containing indican, by macerating them with water, and exposing to the air until fermentation occurs; and the *blue is deposited,* and is formed into hard cubic cakes, which have a copper *lustre when rubbed.* Indigo is insoluble in water, but by action of nascent

hydrogen it takes up two atoms of that element; it is converted into a soluble white powder, *hydro-indigotion*, $C_{16}H_{12}N_2O_2$. By exposing this to the air it again becomes the insoluble blue color. These reactions are taken advantage of in dyeing with indigo, the cloth being steeped in solution of white indigo and then exposed to the air. Indigo blue forms several compounds with strong sulphuric acid, which are generally known in commerce as *sulphate of indigo*.

Indican sometimes occurs in urine, and indigo blue is sometimes deposited from it. It is believed to be derived from indol, $C_{10}H_{14}N_2$, a weak base which is produced by the pancreas.

COMPOUNDS CONTAINING NITROGEN.

The organic compounds containing nitrogen are numerous and present many different grades of complexity, from bodies like cyanogen, CN, which are comparatively easy to understand, up to the intricate materials which form the higher tissues of plants and animals. Nitrogen is susceptible of at least two degrees of valency, triad and pentad, and may sometimes act as monad. It may combine with hydrogen or other positives, may replace hydrogen, or may act in combination with oxygen; in all these ways it gives rise to series of bodies of essentially different character. Carbon and nitrogen form the cyanogen series. Carbon, hydrogen and nitrogen form a group—including many purely artificial products—having alkaline characters. Carbon, hydrogen, nitrogen and oxygen form a group including most of the principles upon which the medicinal and poisonous virtues of plants depend, and also many of the materials forming the tissues of animals and plants. Nitrogen and oxygen, in combination, in the proportion NO_2, constitute a monad radicle, which can easily substitute hydrogen, and thus give rise to a series of artificial substances, of which the chief characteristic is their explosive qualities. We begin the study of the nitrogen group with cyanogen.

CYANOGEN AND DERIVATIVES.

Nitrogen and carbon do not combine if brought in contact, but if a current of nitrogen be passed over a mixture of carbon and potassium carbonate, *potassium cyanide*, KCN, is formed. From this, other cyanides may be obtained. By heating mercuric cyanide, $Hg(CN)_2$, free cyanogen—a compound of equal atoms of carbon and nitrogen—is formed. It is a colorless gas, intensely poisonous. It has but little practical importance in itself, but it forms very important compounds, the nitrogen in cyanogen being

regarded as pentad and the carbon as tetrad; and hence CN will be a monad radicle. It combines with positive and negative bodies. In writing the formulæ of bodies containing cyanogen, the symbol CN is often abbreviated to Cy.

Potassium cyanide, KCN. This body, prepared usually by decomposing some more complex cyanides in the manner described below, is a snow-white mass, very soluble in water, and easily decomposed even by the carbonic acid of the air, hydrogen cyanide being formed. Potassium cyanide dissolves most of the salts of silver which are insoluble in water, except silver sulphide. It is used in silver plating and in photography, also in very small doses as a medicine. It is a powerful poison. It can be melted without change, but in the presence of air or oxidizing agent it turns into an oxygen compound, KCNO, potassium cyanate.

Hydrogen cyanide, HCN. This has been called hydrocyanic or prussic acid, but scarcely deserves such a name. When pure, it is a colorless liquid, easily decomposed and intensely poisonous, a drop or two producing death in a few moments. As sold for medical purposes it is very dilute, consisting of two parts of acid to ninety-eight of water. It has, even when much diluted, a strong odor like that of wild cherry bark or bruised peach kernels. In fact, hydrogen cyanide is formed from these substances, and likewise from other vegetable products, especially from the seeds of many species of rosaceæ (rose family). It does not pre-exist in any of these, but is formed by the decomposition of nitrogenous principles when the seeds are crushed with cold water. This decomposition occurs under the influence of special ferments, for if these ferments are first coagulated by boiling alcohol no decomposition occurs. The reaction by which hydrogen cyanide is formed when, for instance, bitter almonds are macerated with water, is very complicated. It consists in the breaking up of a crystalline principle called amygdalin, under the fermenting influence of a nitrogeneous body called synaptase, as follows :—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\substack{\text{Benzoyl}\\\text{hydride.}}}{C_7H_6O} + \underset{\substack{\text{Hydrogen}\\\text{cyanide}}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$
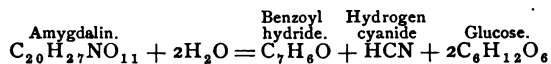
Hydrogen cyanide may also be made by decomposing other cyanides by strong acids, thus :—

$$2KCN + H_2SO_4 = K_2SO_4 + 2HCN.$$
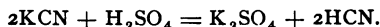
Double cyanides. The cyanides of the potassium group show a great tendency to combine with other cyanides, especially those of the iron group, to form double cyanides, in which some of the properties of the *single cyanides, especially* the poisonous qualities, are completely masked.

The iron series is the most important. We distinguish two well-marked compounds.

Potassium ferrous cyanide, $FeCy_2 + 4KCy$, usually called **potassium ferrocyanide,** and written K_4Cy_6Fe, generally made by heating a mixture of nitrogenous organic matter, iron scraps and potassium carbonate, treating the mass with water and allowing it to crystallize. Large lemon yellow crystals are formed, which are not poisonous. They are much used in dyeing, under the name of yellow prussiate of potash. Oxidizing agents convert the ferrocyanide into ferric, and produce a body called

Potassium ferric cyanide; $Fe_2Cy_6 + 6KCy$, commonly called **potassium ferricyanide** or red prussiate of potash. It forms large ruby red crystals, soluble in water. From these double cyanides others may be obtained. The reactions of these double cyanides with some substances are so distinct as to constitute very delicate tests. With ferrous compounds, for instance, the ferricyanides give a dark-blue precipitate—Turnbull's blue; ferric salts give, with ferrocyanides, a similar blue precipitate —Prussian blue. The two precipitates are nearly identical in composition, $Fe_2(CN)_6 + 3Fe(CN)_2$. An intermediate compound, having the composition $2KCN + Fe_2(CN)_6 + 2Fe(CN)_2$, is known as *soluble* Prussian blue, because it is soluble in pure water, although insoluble in water containing various salts in solution. The true Prussian blue is dissolved by alkalies, but not by acids, except oxalic; a solution made with this acid is used as a blue ink. Prussian blue is much used as a substitute and adulterant of indigo, and for coloring green teas. No precipitate is produced by the action of ferricyanides on ferric salts. That produced by the action of ferrocyanides on ferrous salts is white, but is quickly converted into the blue form by oxidation.

Tests for cyanides. The recognition of cyanogen is a matter of importance in toxicology. The tests can be satisfactorily applied only to the simple cyanides; the double cyanides usually give the reactions after being decomposed by acids.

(*a*) Silver nitrate gives a white precipitate of silver cyanide, which is insoluble in nitric acid.

(*b*) A mixture of ferrous sulphate and sodium hydroxide, when agitated with a cyanide, will produce a Prussian blue, but as this is soluble in caustic soda, it can only be made evident by adding some strong acid.

(*c*) When hydrogen cyanide is brought into contact with ammonium sulphide, a compound called ammonium sulphocyanate is formed, which gives, with ferric chloride, a blood-red color.

Other tests are known, but are of less importance.

Cyanates. Cyanogen being a monad radicle, a single molecule cannot saturate completely the members of the oxygen group, and the compound CNO is, therefore, also a monad radicle. It will combine with potassium. For instance, we have KCNO, potassium cyanate, and so on. Several polymeric isomers of these compounds are known. The potassium series is thus :—

<div style="text-align:center">

KCNO, potassium cyanate.

$K_2C_2N_2O_2$, potassium fulminate.

$K_3C_3N_3O_3$, potassium cyanurate.

</div>

A large number of derivatives have been obtained from these bodies, but only a few are important.

Potassium sulphocyanate, KCNS, is a white, crystalline body, very soluble in water, producing, with ferric salts, a deep blood-red color, which is utilized as a delicate test. Ammonium sulphocyanate, NH_4CNS, is formed when hydrogen cyanide acts on ammonium sulphide, which contains some free sulphur. The reaction is $(NH_4)_2S + S_2 + 2HCN = 2NH_4CNS + H_2S$. This reaction is the basis of one of the tests for cyanogen.

Ammonium cyanate, NH_4CNO. This is one of the most interesting of the derivatives of the compounds of this class, because it is identical in composition, and may be easily converted into *urea*, the most abundant solid constituent of the urine. It may be formed by the action of ammonium sulphate on potassium cyanate, and when heated, either in the solid or dissolved, it soon becomes converted, without change of composition, into a body from which neither cyanic acid nor ammonia can be obtained by the usual tests. This fact shows that the atoms have been rearranged. The body, in fact, has been converted into a substitution ammonium compound, and is identical, in every respect, with urea as obtained from urine.

SUBSTITUTION AMMONIUMS.

Ammonia, NH_3, is always found, either free or combined, among the products of decomposition of nitrogenous matter. As a distinct substance, one of its most striking properties is its power to neutralize acids. It was natural, therefore, that, when organic bodies containing nitrogen were found to have a similar property, a similar constitution should be assigned to them. Hence, morphine, quinine, etc., which, like ammonia, are decidedly alkaline, and contain considerable nitrogen, have been regarded as ammoniacal in character. Although efforts to produce these bodies artificially *have not succeeded, except to* a very limited extent, yet a vast number of

substances resembling them in composition have been obtained, and no doubt need now exist as to the essential nature of these products, or as to the possibility of producing them. The artificial bases now known are produced by the substitution of the hydrogen or nitrogen in ammonia, NH_3, or ammonium, NH_4, by other elements or radicles. The number of compounds so produced is greatly increased by the fact that the molecule of ammonia is capable of polymerism, that is, duplicating itself, so that one set of compounds may be formed on the type NH_3, and another on that of N_2H_6, and so on. A very complete and systematic nomenclature has been adopted for these compounds. In the first place, the character of the replaceable radicles, and, to a certain extent, therefore, the character of the compound itself, is indicated by the termination. When the radicle is positive, and especially when it does not contain oxygen, "*ine*" is used; when negative, and containing oxygen, "ide" is used. When the nitrogen is replaced by some member of its group (P. Sb. As. and B.) some distinct syllables of these names are added. Of course, the names of all the radicles entering into the compound are attached. If the molecule is duplicated, the syllables "*di*," "*tri*," etc., are used to indicate the degree of duplication. If the compound is derived from the type NH_4 it is called an " onium." The following list will show all these points :—

NH_3, amine; N_2H_6, diamine; N_3H_9, triamine; N_4H_{12}, tetramine.

PH_3, phosphine; P_2H_6, diphosphine; etc.   etc.

AsH_3, arsine;   etc.

SbH_3, stibine.

NH_4, ammonium; N_2H_8, diammonium; N_3H_{12}, triammonium.

PH_4, phosphonium;   etc.   etc.

AsH_4, arsonium.

SbH_4, stibonium.

The consolidation of the molecules into diamines and triamines takes place under the influence of radicles of dyad, or higher valency. The methods of producing these substitution compounds are various; one of the simplest is by heating solutions of ammonia with bromides or iodides of the radicles to be substituted. Thus, if ammonia and ethyl iodide be heated for some hours in a sealed tube, we have the reaction

$$NH_4HO + (C_2H_5)I = (C_2H_5)H_3NI + H_2O.$$
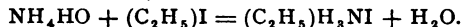
As NH_4I would be ammonium iodide, so the above compound would be called ethyl-ammonium iodide. By further action the whole of the hydrogen may be replaced by ethyl, and we get $(C_2H_5)_4NI$, tetrethyl-*ammonium iodide*. Each one of the hydrogen atoms may be replaced by

a different radicle, and thus great complexity in structure and name arises. Thus:—

$(C_2H_5)_2(C_5H_{11})HNI$, diethyl pentyl ammonium iodide.

$(C_2H_5)_3(C_5H_{11})NI$, triethyl pentyl ammonium iodide.

$(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)NI$, methyl ethyl trityl tetryl ammonium iodide.

From NH_3 we may derive :—

$$(C_2H_5)H_2N, \text{ ethylamine.}$$

$$(C_2H_5)_2HN, \text{ diethylamine.}$$

$$(C_2H_5)_3N, \text{ triethylamine.}$$

When but one-third of the hydrogen is substituted, the body is said to be *primary*; when two-thirds are substituted, it is *secondary*; when all is substituted, the body is *tertiary*. Ethylamine, for instance, is a primary monamine.

Diamines and diammoniums.   These always contain N_2.

$$(C_2H_4)H_4N_2, \text{ ethene diamine.}$$

$$(C_2H_4)H_4N_2(HO)_2, \text{ ethene diammonium hydroxide.}$$

Triamines, and triammoniums, tetramines, and tetrammoniums, are formed on the same principle.

The following formulæ show some of the compounds obtained by these elaborate substitutions, especially when the nitrogen is replaced by other members of its group:—

ethyl phosphine.	diethyl phosphine.	triethyl phosphine.
$(C_2H_5)H_2P$	$(C_2H_5)_2HP$	$(C_2H_5)_3P.$
trimethyl arsine.	triamyl stibine.	triethyl bismine.
$(CH_3)_3As.$	$(C_5H_{11})_3Sb.$	$(C_2H_5)_3Bi.$
	triethyl borine.	
	$(C_2H_5)_3B.$	

tetrethyl phosphonium hydroxide.   tetrethyl stibonium iodide.
$$P(C_2H_5)_4HO. \qquad\qquad Sb(C_2H_5)_4I.$$

By a combination of radicles of different valencies, we may get such a body as

$(CH_3)_3(C_2H_5)_3(C_2H_4)H_4P_3I_3$, trimethyl-triethyl ethene triphosphonium iodide.

NATURAL AMINES AND AMMONIUMS.

The vast majority of the substances indicated in outline, in the preceding paragraphs, are purely products of the laboratory.   Some of them are, *however, identical* with natural products, and many natural products, as *already pointed out, are* so analogous in composition and properties to the

amines, diamines, etc., that no doubt can exist as to their similar nature. A few of these substitution compounds of natural origin, the exact composition of which is known, will be noticed.

Aniline, phenylamine, $(C_6H_5)H_2N$. This body, originally prepared by distilling indigo, is now made very largely by the action of nascent hydrogen on nitrobenzene.

$$C_6H_5(NO_2) + H_6 = C_6H_5H_2N + 2H_2O.$$
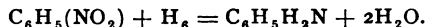
Aniline is a liquid, boiling at 360 F. (182 C.). It is an active poison. By the action of oxidizing agents of different powers, it becomes converted in bodies of complicated composition, some of them triamines, having coloring powers of great beauty and variety, the production of which has given rise to an extensive industry. It appears that, for producing most of these colors, the perfectly pure aniline will not answer; that made from crude nitro-benzene is always used.

Toluidine, $(C_7H_7)H_2N$. There are three isomeric modifications of toluidine, which differ in their fusibility and boiling point. The presence of toluidine in aniline is necessary to fit the latter for the production of some of the aniline colors.

Rosaniline, $(C_7H_6)_2(C_6H_4)H_8N_3$, is a triatomic base, which forms with acids a series of highly colored salts, extensively used in dyeing.

Trimethylamine, $(CH_3)_3N$, occurs in many plants, as in the flowers of the hawthorn and the pear tree, and in wormseed, as well as in different animal liquids. It is a colorless gas, boiling at 48.7° F. (9.3° C.), and smelling of ammonia and fish brine.

AMIDES.

These are produced by the replacement of the hydrogen of NH_3 by acid (negative) radicles. The most important have only one atom of H replaced, and may also be regarded as acids in which hydroxyl is replaced by NH_2.

The following are some amides :—

Acetamide................................. $NH_2C_2H_3O$.
Diacetamide .... $NH(C_2H_3O)_2$

Diamides and higher molecules, also exist as with amines :—

Oxamide (oxadiamide)................. $(NH_2)_2C_2O_2$
Carbamide (carbodiamide)............ $(NH_2)_2CO$

The latter body is *urea*, mentioned above as one of the ingredients of

the urine, and as identical in composition with ammonium cyanate, from which it may easily be formed.

Urea, $C_2H_4N_2O$, is easily crystallized in prismatic crystals, soluble in water and alcohol, and forming with acids definite compounds, among which the nitrate is worthy of notice, as, although soluble in water, it is not very soluble in nitric acid, and hence is sometimes found when nitric acid is added in excess to urine of high gravity. Urea does not displace the hydrogen of acids but combines directly. The formulæ of the nitrate and oxalate are CH_4N_2O,HNO_3 and $CH_4N_2O,H_2C_2O_4$ respectively. Urea is easily decomposed by heat. In the presence of decomposing organic matter it takes up water and becomes ammonium carbonate.

$$CH_4N_2O + 2H_2O = (NH_4)_2CO_3.$$
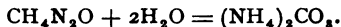
This reaction explains the alkalinity and ammoniacal odor of stale urine.

ALKALAMIDES.

When the hydrogen of NH_3 is replaced partly by positive radicles and partly by negatives, alkalamides are produced. Such a body is $N(C_2H_5)$ C_2H_3O, ethyl acetamide.

ALKALOIDS.

The **natural bases or alkaloïds** are so called because of their power to neutralize even the strongest acids, and form with them distinct and crystallizable compounds. They contain carbon, hydrogen and nitrogen, and, many of them, also oxygen. Their resemblance to the substitution ammonias is obvious, but they are somewhat more complex in constitution, especially as regards the presence of oxygen, which is not an ingredient of the common substitution ammonias. In this respect the alkaloids agree with the amides. Many of them are diamines, some are triamines, some even of higher molecular complexity. By the action of the iodides of the alcohol radicles on them, the number of atoms of unreplaced hydrogen can be determined, and it is shown, by this means, that the majority of the alkaloids are secondary or tertiary amines.

As regards the general properties of the alkaloids, they are mostly solid bodies, not very soluble in water, but soluble in alcohol and easily crystallized. Many have a bitter taste, and decided physiological properties, and are the ingredients upon which the medicinal activity of the plant containing them depends. A few of them are liquid at ordinary temperatures, and those that are solid can be volatilized, without decomposition, by *careful heating.*

LIST OF IMPORTANT ALKALOIDS.

Name.	Formula.	Source.	Properties, etc.
Nicotine	$C_{10}H_{14}N_2$	Tobacco. (Nicotiana tabacum.)	Liquid; boils at 464 F. (240 C.). Sp. gr. 1.027. Soluble in water.
Conine	$C_8H_{15}N$	Water hemlock. (Conium maculatum.)	Liquid; boils at 414 F. (212 C.). Sp. gr. 0.89. It has been prepared artificially.
Lobeline		Indian tobacco. (Lobelia inflata.)	Liquid.
Sophorine		Sophora japonica.	Liquid.
Morphine	$C_{17}H_{19}NO_3$	Opium.	Crystals; slightly soluble in water.
Codeine	$C_{18}H_{21}NO_3$	"	Octahedral crystals; more soluble in water than morphia.
Narcotine	$C_{22}H_{23}NO_7$	"	Crystals; nearly insoluble in water.
Apomorphine	$C_{17}H_{17}NO_2$	By heating morphia with HCl, to about 300 F. (150 C.).	Is distinguished by being emetic, instead of narcotic.

LIST OF IMPORTANT ALKALOIDS.

Name.	Formula.	Source.	Properties, etc.
Quinine..........	$C_{20}H_{24}N_2O_2$		These alkaloids are principally distinguished by their action on polarized light. Quinine, cinchonidine and cinchonicine turn the plane of polarization to the left; Cinchonine, quinidine and quinicine, to the right. They are—except quinoidine, which is a resinous mass—crystalline bodies, not very soluble in water.
Quinidine........	"		
Quinicine........	"	Cinchona bark.	
Quinoidine......	"		
Cinchonine......	$C_{20}H_{24}N_2O$		
Cinchonidine ...	"		
Cinchonicine ...	"		
Hyoscyamine...	$C_{15}H_{23}NO_3$	Hyoscyamus Niger.	Atropia is noted for its power of dilating the pupil of the eye. These are the active principles of well known and important medicinal herbs. They are all powerful poisons.
Atropine.........	$C_{17}H_{23}NO_3$	Atropa belladonna.	
Homatropine ...			
Aconitine........	$C_{30}H_{47}NO_7$	Aconitum napellus.	
Veratrine........	$C_{32}H_{52}N_2O_8$	Veratrum sabadilla.	
Colchicine.......		Colchicum autumnale.	
Strychnine	$C_{21}H_{22}N_2O_2$	Nux vomica.	They form white crystals. Strychnine is less soluble than brucine.
Brucine..........	$C_{23}H_{26}N_2O_4$		
Caffeine..........	$C_8H_{10}N_4O_2$	Coffee, tea and Paraguay tea.	Soluble in water; basic properties feeble; sometimes called theine.

LIST OF IMPORTANT ALKALOIDS.

Name.	Formula.	Source.	Properties, etc.
Theobromine....	$C_7H_8N_4O_2$	Cacao.	Crystals; not very soluble in water.
Piperine	$C_{17}H_{19}NO_3$	Cayenne pepper.	*Yellow* crystals; insoluble in water. Isomeric with morphia, but entirely different in properties.
Pilocarpine.....		Jaborandi.	This alkaloid is distinguished by its power to increase the perspiration.
Pelleterine......		Pomegranate root.	
Physostigmine (Eserine)	$C_{30}H_{21}N_3O_4$	Calabar bean.	Produces contraction of the pupils.
Picrotoxine.....		Cocculus Indicus.	Non-crystalline, and but sparingly soluble in water.
Xanthine	$C_5H_4N_4O_2$	In urine.	
Urea	CH_4N_2O	"	Can be prepared from ammonium cyanate, as elsewhere explained.
Kreatinine	$C_4H_7N_3O$	In urine and juice of flesh.	Can also be formed by the action of strong acids on kreatine, a non-basic principle, existing in juice of flesh.

The majority of the alkaloids form salts by directly uniting with the acid, not by substituting the hydrogen. Thus, morphine forms with hydrochloric acid the compound $C_{17}H_{19}NO_3HCl$; it is, therefore, called morphine hydrochloride, not morphine chloride. We can understand the fact, however, when we recollect that the alkaloids are analogous to NH_3 rather than to NH_4, and the reaction with morphine and HCl is similar to the reaction, $NH_3 + HCl = NH_4Cl$, in which the hydrogen is not replaced. In fact, we might regard the hydrogen of the acid as combining with the morphine, and form a new molecule, $C_{17}H_{19}NO_3H$, analogous to ammonium and called *morphium ;* the compound formed would be *morphium chloride.*

PTOMAINES.

Recent researches have indicated that in decaying animal substances, especially in the early stages of decay, alkaloids are formed which have many properties similar to those obtained from plants. These substances have been called "ptomaines" by Selmi, to indicate that they were of cadaveric origin, but investigation shows that they are probably present in certain pathological conditions, and also normally as a product of change in the living tissue. They are generally amorphous, and of alkaline reaction. Most of them are volatile and easily alterable and form crystalline salts with acids. Allowed to oxidize by contact with the air they emit disagreeable cadaveric or urinous odors. Some ptomaines are not poisonous, but most of them possess strongly toxic properties and cause profound symptoms when injected under the skin.

Ptomaines answer to nearly the same reactions as the vegetal alkaloids, some being precipitated by platinic chloride, gold chloride, mercuric chloride, tannic acid, etc.

Ptomaines are met with :—

1. As a constituent of normal tissues or juices. In this case they are products of tissue metamorphosis.

2. In certain pathological conditions.

3. As a cadaveric or artificial production.

There can be no further doubt that these bodies are largely produced in the process of decomposition of nitrogenous or proteid tissues. They are, however, of slow production naturally, a point to be borne in mind in conducting medico-legal inquiries. Stinking fish, bad meat, etc., all contain poisonous principles, which may be extracted after the manner of ptomaines. The gastro-intestinal irritation and profound toxic symptoms produced by the ingestion of bad food are probably, substantially, processes of alkaloidal *poisoning.*

The ptomaines are not all poisonous. It is common to find a non-poisonous and a poisonous one together in equal proportion. Some are volatile and crystalline, others non-volatile and non-crystalline; some precipitated by ether from acid or alkaline solutions, and some only precipitated by amyl alcohol or chloroform.

Eight classes of ptomaines have been described, the classification being based upon a comparison to the properties of well known vegetable alkaloids.

BIOLOGICAL CHEMISTRY.

Biological Chemistry is the study of the processes of animal and vegetable life. It is a very complicated and difficult subject, and many points are still undecided. Both forms of life require for their maintenance solid and liquid food, and processes of respiration by which gases are absorbed and given out.

VEGETABLE CHEMISTRY.

Plants take their food in the form of unorganized material, and it is distributed in great part by diffusion, as, unlike many animals, they do not have a circulatory system. They are also apparently without any central nervous control, although some plants show irritability and contractility to a high degree. The general nature of vegetable action will be understood by the following sketch of the growth of a plant.

The seed contains an embryo plant, generally with starch. When placed in the soil the embryo begins to grow and the starch is converted into sugar. This serves as nourishment until the roots are sufficiently developed to get the nourishment from the soil. Experiment has shown that good soil contains in soluble form potash, ammonia and phosphoric acid. These the plant takes up by its roots, while the leaves carry on a system of respiration by which carbon is absorbed and oxygen thrown out. The plant thus continually grows. Light, warmth and moisture are necessary for these conditions. The final operation of plant life is the production of the fruit. While this is unripe, it is hard and contains an insoluble body known as *pectose*, together with various acids, tartaric, malic, etc. As the fruit ripens this pectose is changed into *pectin*, which may be still further transformed. Pectin and its derivatives constitute the gelatinizing parts of fruits. The acids are also partly oxidized as the ripening proceeds. After the fruit is ripe it is liable to die and rot. All these processes of growth are accompanied by the production of various proximate principles. The most important of these are, *cellulin*, which constitutes the main framework of all vegetable structure; *starch*, which is deposited in an organized form, and *sugar*, which, being soluble, is found in solution in the fluids. The nature and composition of these principles have *been explained* elsewhere. Other proximate principles of plant life are

resins, fixed and volatile oils, waxes, glucosides and alkaloids. These are all noticed under the proper headings. The proximate principles of plants are generally non-nitrogenous. The nitrogen of plants is principally in the seed.

Chlorophyll. This term is applied to the substance which gives the green colors to plants. It has been much studied, but as yet its composition cannot be said to be definitely made out. Its formation in plants, it is well known, is best seen in the leaves and young stems, especially the former. Light is required for its production, because if plants grow in the dark they remain colorless; but as soon as light is admitted to these colorless structures, the secretion of chlorophyll begins and the plants acquire a green color. It appears also to have some relation to the process of nutrition and respiration, for many plants which are true parasites, that is, live on the elaborated juices of other plants, are either nearly colorless, or have colors different from chlorophyll. An excellent example of this is the *dodder*, a parasitic plant allied to the Morning Glory. It twines around succulent stems, penetrates into their substance and extracts the nutritive juices. As soon as it gets a firm attachment, the parasite loses all connection with the soil and lives entirely on its host. It never forms chlorophyll ; the stem remains of a bright orange color, the flowers are white, and the leaves are not developed. In a considerable number of parasitic plants the leaves are rudimentary. According to some authorities chlorophyll consists of two distinct substances, one of which—cyanophyll—is blue and soluble in ether, the other—xanthophyll—is yellow and insoluble. This opinion, however, is opposed by other observers, who regard the two forms as decomposition products. No definite information can be given as to the chemical nature of the well-known changes which occur in autumn. Some have supposed, as mentioned above, that the green color was due to the mixture of yellow and blue substances, and that the blue decomposed most easily, leaving the yellow, but this is not proved. It is not even known whether the chlorophyll is the same in all plants, nor why some leaves are evergreen and others fade invariably in the autumn.

Solutions of chlorophyll, which may be made by macerating leaves in ether or other suitable solvent, possess a fine green color, and give in the spectroscope several characteristic absorption bands.

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PROXIMATE ANALYSIS OF PLANTS.

The processes for the examination of plants are good illustrations of the methods of proximate analyses, and of the properties of the different groups of organic bodies. Omitting certain preliminaries of drying and ashing, which are for the determination of ingredients that are not strictly organic in character, the processes consist essentially in submitting the plants to the successive actions of a series of solvents. The outline of the method is here given.

The powdered substance is first treated with petroleum spirit—a product of the distillation of coal oil, consisting of the portion which boils below 45° C.—by which means fixed and volatile oils, wax, chlorophyll and possibly alkaloids are dissolved.

Ether is then used, by which are extracted resins and resinoid bodies, fixed oils, if any are left from the first treatment—glucosides, alkaloids and many other bodies.

Absolute alcohol is next used, by which, in addition to many resins or alkaloids that may have escaped solution, tannins and bitter principles are extracted.

Water is then used, by which gums, sugars, many acids and other bodies are removed.

Dilute solution of caustic soda extracts albuminoids, and dilute hydrochloric acid extracts starch and certain mineral substances, especially calcium oxalate.

The residue, after these processes, consists of the wood fibre in various conditions. These are capable of further study, especially by the microscope.

Each of the solutions obtained in the above process consists of a mixture of ingredients which must be separated by special processes.

It is mentioned elsewhere that by treating vegetable matter with a strong solution of caustic soda, under a temperature of 319° F. (154° C.), all the ingredients may be dissolved except the cellulin, which becomes pulpy and easily bleached to a colorless state. This is the method of making paperpulp. The alkaline solution obtained by boiling the wood in this way is of a dark brown color. On the addition of acid it throws down a brown pulpy precipitate, the exact nature of which is unknown. It may be somewhat analogous to the humus or mould which forms when wood slowly decays. An approximation to this result may also be obtained by immersing the more delicate structures, such as leaves or ripe pods, in water, and allowing them to rot. By this means everything softens or decays except *the cellulin* and some of the material which connects its fibres together. It

does not become pulpy, but, retaining its form, presents a skeleton of the original structure.

ANIMAL CHEMISTRY.

The processes of animal life are much more complicated than those of vegetable life. The animal has more functions; its vital action not only produces growth, but also renewal of tissue. The nourishing fluids in many animals are distributed, by mechanical action, to all parts of the body, and every part is under the influence of a central force called a nervous system. The respiration is the reverse of that of the plant, oxygen being taken in and carbon dioxide thrown out. Animal structures are nitrogenous. The chief part of them are classed under the term *albuminoids* or *proteïds*. They are very complicated in composition, containing carbon, hydrogen, oxygen, nitrogen and sulphur, and are, therefore, prone to change, and capable of many modifications. Most of these modifications are capable of existing in both a soluble and insoluble state, and the different forms may be distinguished, to a certain extent, by the conditions under which each becomes insoluble. The important ones are:—

1. Albumin. Blood and white of egg contain this body in the soluble form, but the albumin of blood, ser-albumin, is not exactly like that of white of egg, ov-albumin. A form like the latter occurs in plants. Heat and nitric acid make all these forms insoluble.

2. Globulin. Exists in the crystalline lens.

3. Vitellin. In yolk of egg, in association with fat.

4. Casein. Found in milk. It is not rendered insoluble by heat, but by dilute acids. Considered by some as a combination of albumin with alkali.

*5. Fibrin.* In blood, and chyle, and lymph. Spontaneously coagulable.

6. Peptones. Formed by the action of gastric juice on albuminoids, and are, therefore, the result of digestion. They are not precipitated by acids or alkalies.

Gelatin and Chondin. These are obtained by the action of hot water on skin, tendon and bones. They contain no sulphur. Ordinary glue is a form of gelatin. Like the albuminoids, it exists in a soluble and insoluble modification; the latter form is produced especially by tannin, and upon this property the production of leather depends.

Cholesterin, $C_{26}H_{44}O$, probably $C_{26}H_{48}HO$. This is a non-nitrogenous substance met with in many parts of the body. It is found in bile and blood, also largely in brain and nerve substance. It is a common

product of putrefactive change in muscular tissue. Cholesterin is but slightly soluble in water, but easily soluble in alcohol or ether, from which it crystallizes in pearly plates, showing a somewhat fat-like appearance. It is not a fat, however, being incapable of saponification by caustic alkalies. It is regarded as monatomic alcohol, $C_{26}H_{43}HO$. The radicle $C_{26}H_{43}$ is the twenty-fifth member of a series beginning with C_5H. This radicle is isologous with pentyl. Compounds with acid radicles have been obtained by heating cholesterin with various acids. A sodium compound, $C_{26}H_{43}NaO$, analogous to sodium ethylate, is also known. Cholesterin rotates the ray of polarized light to the left.

Taurin, $C_2H_7NSO_3$, exists in bile, crystallizes in form like quartz, is soluble in cold water, but insoluble in alcohol and ether. In bile it exists, conjugated with cholic acid, as *taurocholic acid*, which is a non-crystalline, resinous fluid, soluble in alcohol and ether, and having a strong acid reaction. Taurin, on the other hand, is neutral to test paper, but is, nevertheless, regarded as an acid in composition. It is amido-ethylsulphonic acid, being derived by the substitution of NH_2 for one molecule of HO in acid ethyl-sulphate, as will be seen by contrasting the formulæ:—

<div style="text-align:center">

Acid ethyl sulphate.   Taurin.

$C_2H_5HSO_4$ $C_2H_5(NH_2)SO_3$

</div>
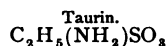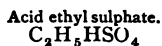
Taurin has been prepared synthetically. There is at least one, and probably two bodies which have the same composition as taurin, but not identical with it. These bodies are not found in animal tissues.

Glycocin, $C_2H_5NO_2$, exists in bile, conjugated with cholic acid, as glycocholic acid. It may be separated by boiling the latter acid with barium hydrate, by which barium cholate is formed, and glycocin set free. It forms hard, granular, somewhat sweetish crystals, but slightly soluble in water. It gives, with strong solution of potassium hydroxide, an evanescent fiery-red color. In composition, it is related to acetic acid, since it may be regarded as derived from that body, by substituting one atom of H by NH_2, thus:—

<div style="text-align:center">

Acetic acid.   Glycocin (amidacetic acid).

$C_2H_4O_2$. $C_2H_3(NH_2)O_2$.

</div>
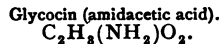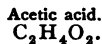
By the action of nitrous acid on a solution of glycocin, it is converted into nitrogen and glycolic acid, $C_2H_4O_3$, which is elsewhere given as a product of the oxidation of ethene glycol.

Leucin, $C_6H_{13}NO_2$. This is found in various organs, and is present, sometimes, in the urine, especially in affections of the liver. It can be *obtained by the* decomposition of albuminoid tissues. For instance, by

boiling horn shavings with dilute sulphuric acid. It crystallizes in white shining plates, soluble in water. It forms compounds with both acids and bases. Its rational formula is $C_6H_{10}(NH_4)_2O_2$, caproic acid, with one H replaced by NH_2, therefore amid-caproic acid.

Tyrosin, $C_9H_{11}NO_3$, is formed from albuminous bodies, at the same time that leucin is formed, by the action mentioned above. It also occurs in the urine, but only in association with leucin. Leucin, itself, sometimes occurs alone in urine. Tyrosin differs markedly from leucin in crystalline form, being deposited in fine, needle-like crystals, which form stellate masses. They are but slightly soluble in cold water; more so in hot. It combines both with acids and bases, forming, however, very unstable compounds.

COMPOSITION AND PROPERTIES OF SOME OF THE SOLIDS AND FLUIDS OF THE ANIMAL BODY.

BONES AND TEETH.

These consist principally of calcium phosphates, $Ca_3(PO_4)_2$, calcium carbonate, and organic matter. The following table gives the approximate proportions:—

	Young child Femur.	Adult Femur.	Adult Tooth.
$Ca_3(PO_4)_2$	50	60	64
$CaCO_3$	6	8	5
$Mg_3(PO_4)_2$	1	1.5	1
Organic matter..	43	30.5	28

The teeth contain about two per cent. calcium fluoride, and other matters not given in the table. The enamel contains only a few per cent. organic matter. It will be noticed that the bones gain in inorganic matter and lose in organic matter as the age advances. Hydrochloric acid will dissolve the mineral matter of bone, leaving the organic. Heated in contact with air, bone burns, leaving the mineral matter as bone-ash.

MUSCULAR TISSUE.

This is nearly three-fourths water, the solid part consisting of fibrin and albumin.

A part of the liquid matter in flesh is the true *juice of flesh*. It has an acid reaction, and contains crystalline organic principles, among which are kreatine, a nitrogenous body related to urea, and inosite, a glucose, together with potassium phosphate and other salts.

BRAIN AND NERVE TISSUE.

These are very complicated in structure. Brain contains about ninety per cent. water; the remainder includes albuminoid bodies, which are partly soluble but mostly insoluble in water, phosphorized bodies, which are regarded as derivatives from phosphoglyceric acid, $C_3H_9PO_6$, various nitrogenous basic principles and inorganic salts.

Glycerophosphoric acid, $C_3H_9PO_6$, may be regarded as glycerin in which one molecule of hydroxyl is substituted by the molecule H_2PO_4. It is, therefore, an acid phosphate. It has been obtained synthetically by the action of glycerin and phosphoric acid, the reaction being as follows:—

$$\underset{\text{Glycerin.}}{C_3H_5(HO)_3} + \underset{\substack{\text{Ortho-}\\\text{phosphoric.}}}{H_3PO_4} = \underset{\text{Glycerophosphoric.}}{C_3H_5(HO)_2H_2PO_4} + H_2O.$$
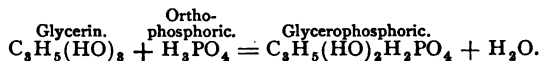
The free acid is somewhat easily decomposed. The phosphorized principles in brain from which phosphoglyceric acid may be obtained, and which are regarded as derivatives from it are, kephaline, $C_{42}H_{79}PO_{13}$, myeline, under which term several bodies are included, and lecithene, $C_{43}H_{84}NPO_8$, which exists in egg matter as well as in brain.

Neurine, $C_5H_{13}NO$, is a basic substance existing in brain and also in yolk of egg. It possesses the general characters of an alkaloid. It can be made to split up into two bases.

Cerebrine. Under this term are included several proximate principles, containing carbon, hydrogen, nitrogen and oxygen. When placed in water they do not dissolve, but swell up very much. They yield glucose when heated with dilute acids, and are, therefore, nitrogenous glucosides.

Hypoxanthine, $C_5H_4N_4O$, and inosite, $C_6H_{12}O_6$, are found in other tissue besides brain. The first is a base. The inorganic constituents of brain are like those of the other tissues and fluids of the body, consisting of phosphates, sulphates, chlorides, etc., but recent researches have shown that copper is generally present, although in minute amount.

BLOOD.

This, as the nourishing fluid of the animal, must contain all the materials necessary for the tissue, and, at the same time, it will always have more or less of the waste material in it. It is, therefore, very complicated. It consists of a clear liquid (liquor sanguinis), holding in *suspension* three forms of corpuscles, red, white and transparent. The transparent form is nearly invisible. The liquid also holds in solution numerous organic and *inorganic substances.*

Elaborate tables have been given of the composition of blood, but the following is sufficient as an outline :—

The liquor sanguinis contains

Water	902.90.
Albumin	78.84.
Fibrin	4.05.
Fat	1.72.
Mineral matter	8.55.
Extractive	3.94.

The corpuscles contain

Water	6.88.
Globulin and cell membrane	282.22.
Hæmatin (including iron)	16.75.
Fat	2.31.
Mineral matter (not including iron)	8.12.
Extractive	2.60.

The term "extractive" includes sugar, urea and uric acid.

The specific gravity of the liquor sanguinis is about 1.028.

The blood is slightly alkaline when first drawn. Soon after leaving the body, the fibrin begins to solidify, and includes in its meshes the corpuscles, forming the clot, and leaving a clear liquid called serum. The cause of this coagulation is not well understood. It sometimes occurs within the body.

Hæmoglobin or *Hæmatocrystalline* is the coloring matter of blood. It is remarkable for containing a small, but constant, amount—about 0.4 per cent.—of iron. According to Kingzett, the analyses of hæmoglobin lead always to the formula $C_{600}H_{960}FeN_{154}S_3O_{177}$. It can be broken up into an albuminous body of unknown composition, and a crystalline sub-stance known as *hæmatine*, $C_{32}H_{32}FeN_4O_6$.

Hæmoglobin may be obtained from blood in a crystalline form. The crystals vary somewhat in different animals, and their formation is pro-moted by light, and by the chemical action of oxygen and carbonic acid on the blood corpuscles.

Hæmoglobin bears a very important relation to the function of respira-tion. It has a purple color in venous blood, but can combine readily with oxygen to form a bright red body—oxyhæmoglobin, the coloring matter of arterial blood. This oxyhæmoglobin parts with its oxygen readily. This accounts for the readiness with which the transfer of oxygen through the blood occurs. Other gases, besides oxygen, are capable of combining

with hæmoglobin. One, carbon monoxide, unites with it so firmly that it cannot be easily displaced. Hence, when carbon monoxide is inhaled, death ensues, from suffocation, because the hæmoglobin is unable to give up the carbon monoxide and take the necessary amount of oxygen.

Hæmin. By rubbing a small quantity of blood with sodium chloride, then boiling it with glacial acetic acid, the mixture, by evaporation to dryness, yields rhombic crystals, to which the composition of $C_{68}H_{72}N_2Fe_2O_{10}Cl_2$ and the names hæmatin hydrochloride and hæmin are assigned.

The albuminous principle in blood is a form called seralbumin. It can be precipitated by boiling, after the addition of a little acetic acid.

The mineral matters in blood are principally sodium chloride, sodium carbonate, potassium phosphate and potassium chloride. Iron is always present, and is found only in the red corpuscles.

The gases of the atmosphere, especially oxygen, are present to a slight extent in blood.

CHYLE AND LYMPH.

CHYLE is the fluid collected from the stomach and intestines, by the lymphatics arising from these organs. It is milk-like during digestion, owing to the presence of minute globules of oil. Lymph is the fluid of the lymphatic system generally, and differs from chyle principally in containing no fat, and both liquids agree in general composition with blood, into which they are finally emptied. Chyle and lymph contain fibrin and are spontaneously coagulable. The analysis of chyle is as follows:—

	In full digestion.	Fasting.
Water	91.8	96.8
Fibrin	0.2	0.09
Albumin	3.5	2.30
Fats	3.3	.04
Extractives	0.4	} .77
Salts	0.8	

It has been calculated that about six and six-tenths pounds of true chyle is formed and poured into the blood during the twenty four hours. The fibrin is not found in chyle as first absorbed from the intestines, and appears to be formed, while passing through the thoracic duct, from the soluble albuminoids present. The extractives include urea, leucine and tyrosin. The salts resemble those of blood. The fats occur perfectly emulsified.

LYMPH is regarded as the serum of the blood, which has been transuded into the tissues and reabsorbed and carried back into the circulation by the lymphatics. It is alkaline in reaction, and consists of a fluid and white

corpuscles, much the composition, therefore, of diluted serum. It is a clear, straw-colored fluid, containing less fibrin and fatty matter than chyle. The fat occurs in globules. The composition of lymph is given as:—

Water	90.25
Albumin	3.50
Fibrin	0.37
Animal extractive	1.56
Fatty matter	3.60
Salts	72
	100.00

MILK.

Milk is a liquid, secreted by a special gland, called the mammary gland, the presence and function of which is characteristic of a class of animals (*mammalia*) the highest in the scale of organic nature as known to us. It consists of a clear liquid, holding in suspension butter fat, in the form of distinct globules, about $\frac{12}{10000}$ of an inch in size, each surrounded by an albuminous envelope. Its composition differs slightly in different animals, but, for the same animal, is pretty constant under all conditions. Cow's milk has been most extensively studied. It and human milk are, of course, the most important. The composition of human milk is erroneously given by most authorities. Dr. Arthur V. Meigs, of Philadelphia, has, by a series of analyses by improved methods, shown that the quantity of casein does not usually exceed one per cent. The following table shows the comparison between cow's milk and human milk.

	Cow's milk. Wanklyn.	Human milk. A. V. Meigs.
Water	88.4	87.2
Fat	4.1	4.3
Sugar	4.4	7.4
Casein	5.2	1.0
Salts	0.7	0.1

The specific gravity of both milks is about 1.032.

The composition of butter-fat, and the general nature of the milk sugar, have been considered elsewhere. Casein is referred to among the albuminoids. The salts of milk are the chlorides and phosphates of potassium and sodium. The reaction of milk appears to be not constant; it is generally, but not always, slightly alkaline. If rendered distinctly acid, the casein becomes insoluble and precipitates, carrying with it most of the milk globules; the precipitate is the curd; the clear liquid, the whey. The rela-

tion, therefore, of fresh to curdled milk is somewhat like that of fresh to clotted blood, the butter globules corresponding to the corpuscles, and the casein to the fibrin. The so-called spontaneous curdling of milk occurs from the milk sugar undergoing the lactic acid fermentation, the casein acting as the ferment. In this fermentation of lactic acid some of the milk sugar is converted into glucose, and this latter may undergo conversion into alcohol. The alcoholic liquid thus obtained is called *koumis*. It was originally made by the Tartar tribes. As will be seen by the table, milk is a perfect diet, containing all the classes of nourishment. Cream is only milk rich in oil globules.

Colostrum, the first secretion of the mammary gland, is peculiar in several respects. It is denser than ordinary, the specific gravity being about 1.045 to 1.050. The fat is aggregated into much larger masses, and albumin is present, sometimes, in considerable amount. The normal milk sometimes becomes albuminous, and acquires a condition of "ropiness."

DIGESTIVE SECRETIONS.

From the mouth to the terminus of the intestine extends an unbroken line of mucous membrane, every point of which possesses secretive powers more or less distinct in different parts. In addition to the various secretions thus introduced, a number of special glands located outside of the limits of the mucous membrane empty, by means of ducts, their secretions into the digestive tract. The first of these is the

SALIVA.

Saliva is the secretion of several glands. It is obtained pure only with difficulty. Human saliva is a turbid, opalescent, viscid, and feebly alkaline fluid, of low specific gravity (1.005). Its composition is given as :—

Water	994.1
Ptyalin	1.2
Mucin	1.3
Fats	1.1
Salts	1.6

Ptyalin is a body not precisely an albuminoid, but somewhat analogous thereto. Its composition has not been accurately determined. Its special function is the power of converting starch into sugar. Its solution is not coagulated by heating. The saliva also contains potassium sulphocyanate, KCNS, the function of which is not known.

While the secretions of the mouth remain alkaline there is a tendency to

deposit lime compounds on the teeth. This constitutes *tartar*, and although it protects the body of the tooth it has an injurious effect on the gums. Under some diseased conditions the secretions of the mouth become acid; tartar is then no longer deposited, and the decay of the teeth is usually hastened.

The average amount of saliva secreted in twenty-four hours is between two and three pints.

GASTRIC JUICE.

Gastric juice is secreted by a special set of glands which are especially excited to action by the presence of food. The secretion is a thin, glairy fluid, of a yellowish tint and somewhat variable in composition. It is, as usually obtained for examination, mixed with some saliva. Its specific gravity is not constant, being generally about 1.010. It does not coagulate on boiling and is less liable to putrefaction than other secretions. The exact amount of gastric juice secreted in a given time and the composition of it is differently given by different authorities, partly on account of difficulty of obtaining it pure, partly because of the want of exact methods of analysis. Two important constituents are, however, characteristic of it, free hydrochloric acid and a nitrogenous ferment, pepsin. Of course, the principal ingredient is water. The following is an elaborate analysis, calculated to 1000 parts:—

Water	975.00
Pepsin and other organic matter	15.00
Hydrochloric acid	4.78
Sodium chloride	1.70
Potassium "	1.08
Calcium "	0.20
Ammonium "	0.65
Calcium phosphate	1.48
Magnesium "	0.06
Ferric "	0.05
	1000.00

Thudichum expresses the composition in less detail, thus:—

Water	994.6
Pepsin	3.0
Hydrochloric acid	0.2

It will be seen that these two tables do not agree. Some observations indicate a variation of from 0.32 to .05 per cent. in the amount of hydro-

chloric acid, the average being about .17 per cent., or 1.7 per 1000. The quantity secreted has been variously estimated at from sixteen pounds to thirty-one pounds in the twenty-four hours. As mentioned above, the characteristic and important ingredients are the hydrochloric acid and pepsin. It appears, however, that other acids are occasionally present, especially lactic acid. The acidity has been ascribed to acid phosphates.

Pepsin. This is a nitrogenous ferment which may be obtained by various methods, from the gastric juice of various animals. It resembles albumin, but is not identical with it. As usually obtained, it is a grayish-white powder, insoluble in pure water, but very soluble in dilute acids. Its important property is its power to render soluble and diffusible albuminous bodies, such as white of egg. The presence of a mineral acid is required for the process. The pepsin is not destroyed in the process, but appears to act only by its presence. The albuminous bodies are changed in forms called **peptones.** The proportion of pepsin required to change a certain amount of albumin is very small. This process is **digestion**; it is exerted with nitrogenous forms of food; the oils, fats, starches and sugars are not affected. The process of digestion is interfered with by the absence of free acid, by a great quantity of it, and by the presence of alcohol.

Peptones. These are products of the action of gastric juice on albuminoids, and are not yet completely understood. They differ from ordinary albumin in having an acid reaction and not being coagulable by heat or mineral acid. They turn the plane of polarized light to the left. The following is given by Kühne as the course of digestion of albumin, under the influence of pepsin and the free acid of the gastric juice. The albumin first breaks up into *anti-albuminose* and *hemi-albuminose.* The former has been also called para-peptone; it is insoluble in water, but soluble in dilute acids. Hemi-albumin, also called a peptone, is not soluble in cold water, but is in warm; also in solutions of sodium chloride. These two bodies are regarded as being formed by the albumin taking up water, in a manner similar to that by which starch is changed into glucose. Peptones sometimes appear in the urine.

The other ingredients of the gastric juice as given above are of no special importance.

· **Abnormal conditions of the gastric juice.** In defective conditions of the system, or when improper food is taken, the gastric juice becomes changed; it then loses some of its normal constituents, or gains abnormal ones, or an excess of the normal. Especially do we see increase of acidity.

This increase is generally due, not to over-secretion of hydrochloric acid, but to the formation of lactic, acetic and butyric acids by fermentative changes in the food. This is the condition which is sometimes called "acidity of the stomach."

BILE.

Bile is secreted by the liver, the largest secreting organ in the body. It is a yellowish-green, viscid liquid, of specific gravity about 1.020. If it be freed from intermixed mucus it loses its viscidity and shows but little tendency to putrefaction. It has a bitter taste and an alkaline reaction. The composition of human bile is thus given by Frerichs, from an analysis of a sample taken from the gall bladder of a man killed by an injury :—

Water	85.92
Inorganic salts..	.78
Mucous pigment...	2.98
Bile salts..	9.14
Fat...	.92
Soaps ⎫ Cholesterin ⎬ .... Lecithin ⎭	.26

The quantity secreted is estimated at about forty ounces in twenty-four hours. This is all poured into the intestines, but the greater part of it is reabsorbed.

An important property of bile is its reaction with fatty substances. It emulsifies them, that is, breaks them up and renders them miscible with water. A drop of cod-liver oil, for instance, mixed with a drop of bile, is converted into a milky liquid. By such action the fatty matters of the food are subdivided sufficiently to allow of their absorption by the lymphatics of the intestine. It has also been stated that the bile has the power to convert starch into sugar. In the intestinal canal bile is supposed to act, in addition to its digestive functions, also as an antiseptic and mild stimulant to the muscular-coat.

The inorganic constituents of bile are water, chlorides and phosphates, and need no special mention. The principal organic constituents are sodium glycocholate and taurocholate, cholesterin, and several pigments. It contains no albumin. The glycocholate and taurocholate can be decomposed by sulphuric acid and the free acids thus obtained. Although not existing in bile in the free state, their properties are of interest, and have been alluded to in connection with the descriptions of taurin and glycocin. Taurocholic acid contains sulphur; glycocholic acid does not.

Cholesterin, another important ingredient of the bile, is elsewhere described.

Bile pigments. Several bile pigments exist. Three have been distinctly indicated and analyzed, viz.: *bilirubin, biliverdin,* and *bilifuscin.*

Bilirubin, $C_9H_9NO_2$. This is, according to Thudichum, a monobasic acid, and exists in bile in the form of a calcium salt. When liberated by the action of acids it forms a powder of a brilliant red color, insoluble in water, alcohol and ether, but soluble in chloroform. Nitric acid containing nitrous acid produces with bilirubin a play of colors, from green, through blue, violet and red, to yellow. This reaction is utilized as a means of detecting traces of bile in organic fluids. Bilirubin is supposed to be the substance which gives the yellow color to the skin in jaundice.

Biliverdin, $C_8H_9NO_2$. This coloring matter is produced when bilirubin is dissolved in caustic alkali and exposed to the action of oxygen for some time. The solution, at first red, finally turns green, and on the addition of hydrochloric acid a green precipitate is produced. The reaction of its formation, therefore, consists in the removal of one atom of carbon from bilirubin.

Bilifuscin, $C_9H_{11}NO_8$. This coloring matter can be obtained directly from bile or from gall stones. Its composition is a little uncertain. It appears to be an acid like bilirubin.

The other coloring matters will not need description.

Sodium taurocholate and glycocholate give, with a mixture of sulphuric acid and sugar, a violet color, which has been called Pettenkoffer's reaction. It was at one time supposed that bile products were the only ones that would give this, but other bodies which give it are now known. Still, under proper care, this reaction is a good test for the presence of bile. Some substances give the reaction with sulphuric acid alone, but these are nearly all glucosides, and under the influence of the acid they yield the glucose which is necessary for the test.

PANCREATIC SECRETION.

Pancreatic juice is a viscid alkaline secretion, of a specific gravity about 1.008. It contains about ten per cent. of solids, and, unlike bile and gastric juice, is very liable to putrefaction. Its functions are somewhat similar to those of the saliva; the pancreas has been called by physiologists the abdominal salivary gland. The exact composition of pancreatic juice is not yet made out. The following is given as an approximation:—

Water 90.07
Organic matter.. 9.04
Sodium chloride... 0.73
Free alkali.. 0.03
Sodium phosphate... 0.04
Sodium sulphate............................. .... 0.01
Other inorganic salts... 0.08

The organic matter is principally soluble albumin and alkaline compound of albumin; also a special ferment, pancreatin.

The amount secreted is small; about five ounces in the twenty-four hours.

The special chemical actions of the pancreatic juice are, to convert starch into sugar and to emulsify fats. A preparation of its special principle, pancreatin, is now used for the purpose of making emulsion of cod-liver oil for therapeutic purposes.

THE INTESTINAL JUICES.

In addition to the digestive secretion considered above, the glands of the intestines throw out secretions amounting, according to some authorities, to ten ounces in the twenty-four hours. Very little is known of the composition of these secretions, on account of the difficulty of obtaining them pure and in sufficient quantity. Some writers have described the intestinal juice as a viscid, transparent, alkaline secretion, which is coagulated by some substances, and contains from two to two and a half per cent. of solids. Its chemical action on the food is supposed to be about the same as that of the pancreatic juice.

EXCRETIONS.

A considerable number of products formed in the animal system are of such a character that they must be removed sooner or later from the body, or injury to health will result. For some of these the special secretory organs are provided, and, consequently, such products are both secretions and excretions. Two of these will be here considered: sweat and urine; the first the secretion of the skin, the second, of the kidneys. The two organs stand to each other in a vicarious relation; that is, one is capable, to a certain extent, of performing the functions of the other; but this substitution is not perfect.

SWEAT.

This term includes only the fluid portion of the secretion, but experiment has amply demonstrated that carbonic acid gas is also given out, although only in small proportion. The water, for the most part, passes off in an insensible form, being carried away in solution in air surrounding the body; but when this air is saturated with moisture, or when the secretion of sweat becomes much increased, the water accumulates on the surface of the skin in the form of drops. From various experiments it has been concluded that the amount of water passed off by the skin in twenty-four hours is about two pounds; the amount of carbonic acid is only about $\frac{1}{75}$ of that given off by the lungs. Very little is known about the solid contents of the sweat. Its composition is probably variable, even within the limits of health, and undoubtedly considerable changes take place in disease. In the normal state it contains free lactic acid. The results of analyses have been represented as follows:—

Water	995.00
Epidermis and calcium salts	.10
Bodies soluble in water	1.05
Bodies soluble in alcohol	2.40
Acetates and lactates	1.45
	1000.00

It is obvious that this statement is unsatisfactory.

URINE.

The urine is the most important and abundant of the true excretions, and has, perhaps, been more extensively and accurately examined than any of the animal fluids. It is quite complicated in composition, but many of the substances are present only in small amount. A few of the substances it contains are almost characteristic of it, although found in small amounts in other fluids.

Characteristics of Normal Urine. It is a clear, pale yellow or amber-colored fluid, of acid reaction and well known characteristic odor. Its specific gravity varies considerably, even within the limits of health, and in diseased conditions a wide range of gravity is noticed. Normal urine may vary from 1.018 to 1.030. The quantity passed in the twenty-four hours is not constant, and is variously given by different authorities, but fifty fluid ounces—about fifteen hundred cubic centimetres—

is probably a fair average. If the quantity of water taken into the system is large and the skin is prevented from acting, the amount of urine secreted increases and the specific gravity falls, and under opposite conditions the gravity rises. The following table, giving minutely the composition of normal urine, is from Kingzett.

Average composition of normal urine passed during twenty-four hours by an adult man weighing 140 pounds—

Urea..	30 to 40	grams
Uric acid..	0.5	"
Kreatine...	0.3	"
Kreatinine	0.45	"
Hippuric acid......................................	0.5	"
Acetic acid..	0.288	"
Formic acid..	0.050	"
Kryptophanic acid..................................	0.65	"
Sodium and potassium chlorides...............	10 to 13	"
Sulphuric acid (as sulphates)................	15 to 25	"
Other sulphur compounds..........................	0.2	"
Phosphoric acid (as phosphates)...................	3.66	"
Lime..	.17	"
Magnesia..	.19	"
Ammonia...	0.70	"
Bile acids..	0.012	"

In addition to these ingredients many others are given as present in unestimated and very minute amounts.

A succinct account of the methods of examining urine for purposes of diagnosis is given in another section. It will be sufficient here to describe briefly a few of the specific proximate principles contained in it.

Urea, CH_4N_2O. This is almost always present in the urine, and except in disease, is its most abundant solid constituent. As it is found in the blood, it is believed to be only secreted by the kidneys from that fluid, not formed by them. It is isomeric with ammonium cyanate, $(NH_4)CNO$, and can be formed from it. Its rational formula is generally given as $(CO)H_4N_2$, being diamine H_6N_2 in which two atoms of hydrogen are replaced by the acid radicle (CO). It ought, therefore, to be called carboxene diamide; it is generally, however, called more briefly *carbamide*. It is a colorless, easily crystallizable solid, soluble in its own weight of water; also soluble in alcohol. It is decomposed by heat and by many chemical agents. In the presence of putrefying or fermenting sub-

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stances it takes up two molecules of water and becomes ammonium carbonate.

$$CH_4N_2O + 2H_2O = (NH_4)_2CO_3.$$
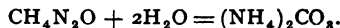
The reaction does not occur with a pure solution of urea in water, but quickly occurs in ordinary urine, on account of the decomposition of the mucus. By this reaction stale urine becomes alkaline. With sodium hypobromite or hypochlorite, urea is decomposed, most of its nitrogen being given off in the free state.

Urea is a base forming a series of well marked salts, in which, as in the case of the organic bases generally, the acid unites without loss of hydrogen. Urea nitrate, for instance, is CH_4N_2O,HNO_3, and urea oxalate is $(CH_4N_2O)_2H_2C_2O_4$. Both of these salts are but sparingly soluble in water. Urea also combines with mercury oxide and with mercury nitrate. It exists in the urine in the free state.

It is believed that urea is formed in the blood by the decomposition of albumin.

Uric Acid, $H_2C_5H_2N_4O_3$. This appears to occur in the excretions of most animals, and is especially abundant in that of reptiles. It is contained in human urine only in small quantity in health, but in certain diseased conditions of the system the quantity increases, and it becomes a source of local trouble. It is a very common ingredient of urinary calculi and deposits. It probably exists in combination in human urine. Uric acid, when pure, is a white, crystalline powder, almost insoluble in cold water. It forms two classes of salts, acid and normal. They are, in general, more soluble in water than the free acid; lithium urate is one of the most soluble. The normal urates are easily decomposed. When uric acid or urates precipitate from urine they generally carry down with them some of the coloring matters of the liquid. By the action of hydrating and oxidizing agents on uric acid a great variety of interesting products is formed which throw light on the nature of the acid. By oxidation under certain conditions it forms urea, and this fact has given rise to the supposition that the uric acid found in the urine is only a portion of that which is really formed in the system, the greater portion having been oxidized to urea. It is also inferred that when uric acid is excreted in excess it is due to the defective oxidation. Normal urine passed during twenty-four hours does not contain more than eight grains.

Xanthene, $C_5H_4N_4O_2$, which differs from uric acid only by having one less atom of oxygen, is present in small amount in normal urine. Very rarely it is encountered as a form of calculus. It forms white, amorphous

granules, and yields compounds with acids. The hydrochlorate is $C_5H_4N_4O_2HCl$.

Hippuric acid, $HC_9H_8NO_3$. This substance is present only in small quantity in human urine, about one gram being passed daily. Vegetable diet increases the quantity, and hence in the urine of herbivorous animals it is an abundant ingredient. It crystallizes in prisms which are but slightly soluble in cold water. The solution has an acid reaction. It is decomposed by heat and by boiling with acids, yielding benzoic acid or allied bodies. Thus, by boiling with dilute acid we get the following, a molecule of water taking part in the reaction :—

$$\overset{\text{Benzoic acid.}}{} \qquad \overset{\text{Glycocin.}}{}$$
$$HC_9H_8NO_3 + H_2O = HC_7H_5O_2 + C_2H_5NO_2.$$
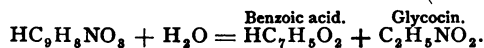
A similar decomposition will take place under the influence of nitrogenous ferments, and thus the putrid urine of horses and cows may be made to yield large amounts of benzoic acid. These reactions indicate that the rational formula of hippuric acid is $C_2H_4(C_7H_5O)NO_2$, benzoyl glycocin.

MUCUS.

Mucous membrane is continuous with the skin and somewhat like it in structure. It is kept moist by a secretion called *mucus*. This is a tenacious fluid which is not perfectly miscible with water. The tenacity is given to it by a non-sulphuretted, albuminous body, called mucin, which is precipitated by alcohol and dilute acids. Mucus contains corpuscles. The following analysis is due to Berzelius :—

Water	933.7
Mucin	53.3
Alkaline lactates	3.0
" chlorides	5.6
Extractives	7.4

PUS.

Pus is a pathological product and may be produced by irritation of a mucous membrane. It consists of two portions, a clear liquid, *liquor puris*, and corpuscles very much like the white corpuscles of the blood, and still more like those of mucus. The corpuscles yield several albuminous principles; the *liquor puris* contains also several forms of albumin. Pus is mostly but not always alkaline in reaction. In general composition it bears some resemblance to blood, but it varies much. The composition of

pus has been given as: Water, 87; proteids, 8.5; fatty matters, 3.0; extractives, 0.7; salts, 0.8. The nuclei of the corpuscles appear to contain a phosphorized principle.

CLINICAL EXAMINATION OF URINE.

APPARATUS REQUIRED FOR URINARY ANALYSIS.

For the ordinary clinical examination of urine comparatively little apparatus and chemicals are required.

One dozen test-tubes, best quality, about 4 inches long, some wide, others rather narrow. Test-tubes on feet are of little use.

Small spirit lamp. Wood spirit, methyl alcohol, may be used in this. It is cheaper than common alcohol.

Test-tube holder. The ordinary clothes-line clip will answer if the power of the spring is considerably diminished by cutting off about half of it.

Several wine glasses. The interior should be sharply conical. These are used for collecting sediments.

Rack for holding test-tubes.

Glass tubes about six or eight inches in length and less than ¼ inch external diameter, cut squarely off at each end. These are used as pipettes to withdraw sediment.

A urinometer and jar.

A few watch glasses.

Glass rods, narrow and about six inches long; the ends should be rounded in the spirit lamp.

Several funnels, about 1½ inches across the top. A good funnel has its sides at an angle of sixty degrees and making a sharp angle with the stem. These are sold as analytical funnels.

A piece of platinum foil, about an inch square.

Litmus paper. The method of preparation and use is given below.

Filter paper. Good German paper will generally answer; Swedish No. 2 is a better grade.

Pure nitric acid.
Brown fuming nitric acid.
Pure hydrochloric acid.
Pure sulphuric acid.
Pure acetic acid.

These should be kept in one-ounce glass stoppered bottles. The labels may be kept from corrosion by a thin layer of paraffin.

Solution of caustic soda. This should be quite strong, and may be kept in a rubber-stopped bottle.
Solution of ammonia.
  " barium nitrate.
  " silver nitrate.
  " copper sulphate.
Bismuth subnitrate.

The preparation of a number of other special solutions are described in connection with the special use made of them.

QUALITATIVE ANALYSIS.

The secretion from the kidneys is a complex solution of organic and inorganic constituents. Within the limits of health it is tolerably constant in composition, the principal variation being with reference to the proportion of water. The general chemistry of the urine and a statement of the elaborate analysis has been given elsewhere.

Under conditions of disease, not only of the kidneys but of the system at large, great variation in composition occurs. For practical purposes we may arrange these changes under three heads :—

1. Marked diminution in quantity or entire absence of any ingredient.
2. Marked excess of any ingredient.
3. Presence of substances not found in normal urine.

Absolutely reliable observations can only be made on samples that are less than twenty-four hours old.

Normal urine is a clear, light amber-colored liquid, of acid reaction and characteristic odor. The specific gravity varies from 1.015 to 1.028, and is generally about 1.020; both it and the color are usually dependent on the proportion of water. When the kidneys are not acting well, or when, as during the warmer season, much water is being excreted by the skin, the specific gravity and color will increase; on the other hand, when the kidneys are stimulated, or when, as in cold weather, perspiration is checked, the specific gravity and color will decrease. Practical knowledge of the effect of these conditions can best be obtained by a few experiments on one's own person. If on a warm summer's day a person takes a hydragogue cathartic it will be found that so much more water will be excreted by the bowels and the skin that the operation of the kidneys seem almost suspended. An opposite effect will be produced by a diuretic. After a few doses of digitalis, for instance, a considerable amount of pale urine will be passed. Many alcoholic liquors have a similar effect. In all these instances the ratio between the solid substances remains the same. The condition is

materially different from that in disease, in which alterations of color and gravity are due to increase or diminution of one substance or class of substances.

Specific gravity is generally taken by means of a urinometer, which is a graduated bulb-tube weighted so as to float upright. Extreme accuracy is of no service, a difference of a few degrees not signifying anything clinically. In using the urinometer the following precautions are necessary :—

(*a*) The urine must be at a temperature near 60° F.; the determination should not be made when the liquid is first passed.

(*b*) The instrument must be placed in carefully, and the glass vessel must be wide enough to allow it to float freely.

(*c*) In reading the gravity the eye should be placed on a line just below the level of the liquid. This is to avoid the error due to the curved line which the liquid makes with the graduated stem. For instance, in the

annexed diagram

the reading should be along
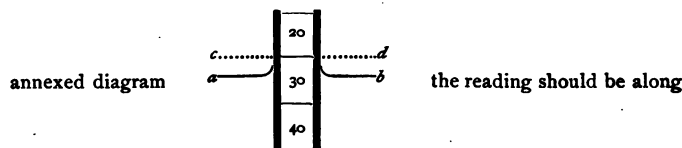
the line *a b*, not along *c d*, which latter is only the apparent level.

The cheaper forms of urinometers are usually quite sufficient for clinical purposes. In addition to the figures, the scales sometimes bear letters, A for albumin; S for sugar, etc. No attention should be paid to these. It is advisable to test each one by placing it in ordinary hydrant water at a temperature of 60° F. and noting whether it sinks to the 1000 mark.

The figure for specific gravity may be made the basis of a rough determination of the solids excreted; by multiplying the last two figures by 2 we get approximately the number of parts of solid per 1000 of urine. Thus a specific gravity of 1.020 would give us 20 $\times$ 2 = 40 parts per 1000, *i. e.*, 4 per cent. 1.030 would give 60 per 1000, *i. e.*, 6 per cent.

Reaction. Urine, when fresh, is generally decidedly acid, due most probably to acid sodium phosphate, but when uric and hippuric acids are in excess they may also contribute to the acidity. The acid reaction increases slightly after the urine has been passed, but very soon the mucus begins to decompose and causes the urea to become ammonium carbonate. The liquid becomes alkaline and very foul smelling. A neutral condition or transient alkalinity is seen in the urine secreted just after a meal, and an alkalinity due to decomposition is noticed in those cases in which, owing *to obstruction,* the liquid is retained in the bladder for some time.

For determining reaction, litmus paper is entirely suitable. A solution of litmus is prepared by boiling it in water; this is divided into two parts, to one of which some strong acid is added, drop by drop, until the color is wine-red. This is then mixed with the other half of the liquid. Slips of filtering paper are dipped in this liquid and dried. They will assume a purple tint and are very delicate, responding either to a trace of free acid or of alkali. By employing this form of paper we avoid the necessity of using two colors. The paper should be cut into pieces about one-half an inch square, one of these being dipped into the sample to be tested. Of course, no piece should be used a second time. Litmus *paper* is best kept in a closed bottle away from the light, but litmus *solution* must be kept in an open bottle. It will then keep for a long time, while in a closed bottle it will soon decompose.

Measure of acidity. The acidity of the urine may be quantitatively expressed by comparing with a solution of oxalic acid. It normally has, in the twenty-four hours, an acidity equal to between 1.5 and 2 grams of oxalic acid. A solution of oxalic acid containing 1 gram in 100 c.c. (or 10 grains in 1000 grains) of water is first prepared, then a solution of caustic soda of about the same strength. A definite amount of the oxalic acid is then colored with litmus, and the solution of soda run in slowly from a graduated vessel until the litmus is just turned blue. The experiment is then repeated with a measured quantity of urine, and the comparison can at once be made. Thus, suppose 25 c.c. of oxalic acid solution taken, corresponding to 0.25 gram oxalic acid, requires 25 c.c. of soda solution to neutralize it, and a similar soda solution neutralizes 200 c.c. of urine, then it is clear the 200 c.c. of urine has an acidity equal to 0.25 of oxalic acid.

Color. The urine varies from a very pale, almost colorless, liquid to a dark amber color. The presence of blood gives it a smoky hue. The spectroscope shows in normal urine the existence of an absorption band coincident with that seen with *choletelin*, one of the pigments of bile. It seems that the principal urinary pigments are of biliary origin, but some of them originate from the blood. Indican, which has been regarded by some as a combination of glucose and indican, and, therefore, a glucoside, is generally present. It is supposed to be one of the bodies which give to the urine the power of responding to the sugar tests. Several tests are given for the identification of these ordinary matters, but the clinical significance of their deficiency or excess is not yet made out.

The substance which is allied to choletin is known commonly as *urobilin*, and is especially abundant in the high-colored urine of fever. The follow-

ing tests may be utilized for observation as to the amount of urobilin and analogous bodies :—

Ammonia is added to the urine until it is distinctly alkaline, and then zinc chloride. If urobilin is present in considerable proportion a fluorescence will be noticed, and the characteristic absorption band—between b and F —will be seen.

In urine containing the color in normal amount strong sulphuric acid produces a deep garnet-red tint. If the coloring matter is in excess the sulphuric acid mixture is black and opaque; if deficient, the mixture is pale ruby red. The test is best applied by allowing the urine to fall, in a fine stream, from a height of about four inches upon some strong sulphuric acid in a test-tube. The urine should be allowed to mingle with the acid. If sugar, blood or bile products be present a reaction simulating excess of coloring matter will be given.

Nitric acid, added to about four times its bulk of the liquid to be tested, will give very little tint when the coloring matter is normal, but if present in excess red or purple tints will be produced. The urine should be either diluted or concentrated, as the case may be, until the quantity passed in the twenty-four hours equals sixty ounces.

Indican may be recognized by its reaction with hydrochloric acid. This produces in normal conditions only a pale yellowish-red color, but larger quantities produce a violet or blue coloration. The test is generally made by adding about a drachm of urine to ten or twenty drops of strong hydrochloric acid, stirring the mixture. A small quantity of nitric acid increases the delicacy of the test. Bile products interfere with the value of this test.

Another method is to mix the urine with an equal quantity of the strongest hydrochloric acid, and then, drop by drop, shaking constantly, a solution of so-called chloride of lime, until a deep blue color is produced. The liquid is then shaken with chloroform, which will separate as a blue fluid, more or less deep in color, according to the amount of indican present.

Abnormal coloring matters. These include various modifications of the blood-coloring matters, a special color known as uroerythrin, biliary products and color due to articles of food.

Blood colors. These give to the urine a smoky color when in small amount; larger quantities color it red.

When blood itself appears in urine the corpuscles may be recognized by the microscope, and the condition is called *hæmaturia,* but if only the coloring matters of the blood are present the condition is called hæmati-

nuria. In the latter case the abnormal ingredients are recognized by spectroscopic and chemical methods. Absorption bands are seen mostly between D and E, and one near C. The chemical test is to add to the liquid a small amount of tincture of guaiacum and a few drops of ether containing hydrogen dioxide. If blood products be present a blue color will be imparted to the ether. The ethereal solution of hydrogen dioxide may be prepared by adding barium dioxide to slightly diluted hydrochloric acid and shaking the mixture with ether. Hydrogen dioxide is formed, and taken up by the ether, which may be easily decanted from the acid liquid. The solution does not keep very well.

Biliary coloring matters. When these are present in decided amount they give a yellow color to the urine. The chemical reaction for them is that fuming nitric acid—often sold by druggists under the name of *nitrous* acid—gives a series of colors in the order, green, blue, violet and yellow. The green color at the beginning is especially typical. A mixture of sodium nitrate and sulphuric acid will also answer. The test may be performed in a test-tube in a manner similar to that described in testing for albumin—Heller's test—or by placing on a plate a drop or two of the urine and of the test liquid, and allowing the two to mingle slowly.

The bile-acids may be present in urine, but are not common, and the test for the biliary coloring matters will generally be sufficient for clinical purposes.

Variations in the inorganic constituents of urine. The inorganic constituents of the urine that have the most clinical importance are the chlorides and phosphates.

Chlorides are diminished during febrile conditions; sometimes entirely absent. They may be at once recognized by adding a few drops of nitric acid, and then silver nitrate. A white precipitate is at once formed if chlorides are present.

Phosphates. Potassium and sodium phosphates are called alkaline phosphates; calcium and magnesium phosphates are called earthy phosphates. The former are soluble in water; the latter not; both are soluble in acids.

The amount held in solution depends in part on the amount of acid, also on the temperature. These facts are important, because a deposit of phosphates may occur, either from alkalinity or deficient acidity of the urine, or from actual excess of the phosphates themselves. The clinical significance of these conditions is, of course, very different. By means of litmus, as already given, the reaction of the liquid can be easily ascertained. Deposits

of phosphates are generally bulky and white, remaining undissolved when the liquid is boiled—being thus distinguished from urates—but dissolving in hydrochloric or nitric acid. Such deposits have no significance when found in urine which has become stale and has thus acquired an alkaline reaction.

Phosphates are deposited in various forms, which are, in the main, distinguishable from each other and everything else by the microscope.

Oxalates. Calcium oxalate, CaC_2O_4, is the only one requiring notice. It is deposited in the minute but very distinct octahedral crystals and also in dumb-bell forms. These crystals are soluble in the mineral acids, but not in alkalies or acetic acid. The clinical significance of calcium oxalate is not well understood. It is easily produced by the eating of various vegetables, especially the common garden rhubarb, and its occurrence appears to have some relation to dyspeptic conditions. Not infrequently it is found associated with traces of albumin.

Uric acid. Excess of uric acid is usually shown by a brick-red deposit of small crystals. Under the microscope, even with a low power—40 to 60 diameters—these show various forms, generally lozenge-shaped. Uric acid is bibasic, and, therefore, forms both acid and normal urates. Both forms are but slightly soluble in water; the acid urates are much less soluble than the normal. The solubility of all the forms, as well as of the acid itself, is increased by heat. The urates, like the acid, carry down with them some of the red coloring matter of the urine. They are not as distinctly crystalline as the free acid.

A deposit of urates may be recognized by the red color, and by dissolving in whole or in part by heating the liquid in which it is suspended.

Uric acid, or any of its compounds, may be recognized by the so-called *murexide test*. The sediment is treated on a watch glass or cover of a porcelain crucible, with a drop or two of nitric acid—not very strong—and then carefully evaporated to dryness. A drop of ammonia is then added, and if uric acid was present a purple color will be produced.

Another test is to treat a little of the substance to be tested with potassium carbonate, moisten a piece of filter paper with this solution, and then add a little silver nitrate solution. Uric or urates, if present, produce at once a gray stain.

Albumin. It is doubtful if albumin ever appears in the urine in a state of health. Some authorities have so asserted. It is sure, however, that it is, in the majority of cases, even when in small quantity, a concomitant and indication of disturbance, either local or general. It must be borne in

mind that it is by no means always a sign of kidney disease. Change of blood pressure in the kidneys, escape of pus or blood into the urinary apparatus, will give rise to the presence of albumin. It becomes of special significance when it is associated with " casts," for the recognition of which the microscope is required. The tests for albumin are all dependent on its coagulation. The liquid should always be filtered before the tests are applied and its reaction noted. If alkaline, and especially if carbonates are present in considerable amount, the liquid may be mixed with about one-fourth its volume of caustic soda solution, warmed a little and filtered. If the filtrate is not clear a few drops of a solution containing magnesium sulphate, ammonium chloride and ammonia should be added and again filtered.

HEAT. Albumin is rendered insoluble by a heat of about 150° F. (65° C.), especially in the presence of free acid. Alkaline solutions are some·times difficult to coagulate. In the practical application of the heat test a test-tube should be about one-third filled with the urine and boiled for a few seconds, and then, whether a precipitate is produced or not, a few drops of nitric or acetic acid should be added. If a precipitate remains after the addition of the acid the presence of albumin is indicated. A precipitate produced by boiling but dissolved by the acid is due to phosphates and may be disregarded.

NITRIC ACID, HELLER'S TEST. This acid produces coagulation in the cold, and gives us a method but little liable to fallacy. About fifteen drops of commercial nitric acid are placed in a somewhat narrow test-tube, and about a drachm of urine poured slowly down upon it, holding the tube considerably inclined. Another method, and one preferred by many, is to put the urine in first and pour the acid down the side of the inclined tube, when it will run below the urine and form a clear layer at the bottom of the tube. Both liquids can be conveniently introduced by a pipette. Under either method the albumin will coagulate at the point where the acid and urine touch, and will form a white ring or cloud, the density and distinctness of which will depend upon the amount of albumin present. The effect is produced quickly and is best seen by holding the tube in front of and a few feet distant from a white ground, as the frame of a window, and shading slightly the lowest point of the tube.

Fallacies. Urine rich in urea sometimes gives a precipitate of urea nitrate, which might be mistaken for albumin. It can be distinguished by its solubility when warmed, and by its crystalline character.

Excess of urates may also produce a misleading precipitation, but the ring produced by these is generally more irregular and after a few hours is

converted into the crystalline uric acid, which is easily recognized under the microscope.

In exceptional cases resinous bodies which have been given as medicines may be found in the urine in soluble combination with the bases present. Such compounds may be decomposed by the acid and the resin precipitated as an amorphous mass, which may simulate albumin. The distinction will be the odor of these resins and their solubility in strong alcohol. In addition to these points, the fact of their being administered will suggest precaution in regard to the test.

GLACIAL PHOSPHORIC ACID (Metaphosphoric acid, HPO_3). The fact that this body will coagulate albumin has long been known, but it has been but little used in testing urine. I called attention to its use at a meeting of the Philadelphia County Medical Society, held September 21st, 1881. It is sold by druggists in the form of white or transparent sticks, and is used by simply breaking these into fragments and dropping one of them into a test-tube containing a convenient amount of the urine. As the acid dissolves it precipitates the albumin in the form of a dense cloud, which can be diffused by shaking. If the acid be kept in small fragments, in a *tightly stopped* bottle, it is very easy to apply the test, and as far as I have experimented with it, it is more delicate and as trustworthy as the nitric acid test. A quantity of the solid acid as large as a pea is sufficient for a fluid drachm of urine. Heat should not be used. The acid may be dissolved in water and in glycerine, but the solution must be made without heat and used at once, as it is liable to change into orthophosphoric acid, H_3PO_4, which is inactive.

If the urine contain alkaline carbonates the addition of the phosphoric acid will cause effervescence. The acid will, however, soon neutralize the alkalinity of the urine, and produce a coagulum if albumin be present.

Numerous tests for albumin have lately been announced, some of which have no advantage over older methods, but others are decidedly more delicate. The tests are used in watery solution, and are all applied in the same manner as the nitric in Heller's test, that is, by making the urine float upon the test solution, when if albumen be present a white ring of coagulation will form. Citric acid is used with the tests, being either added to the test liquid or to the urine. (See Appendix.)

POTASSIUM FERROCYANIDE in saturated solution.

POTASSIUM MERCURIC IODIDE, made by mixing 18 grains of mercuric chloride, 50 grains potassium iodide, and 3 ounces of distilled water.

SODIUM TUNGSTATE. Saturated solution.

PICRIC ACID. Saturated solution containing also two drachms of citric

acid to the ounce   This is considered a delicate test, but is liable to some objections and fallacies.   It stains the skin a strong yellow and gives precipitates with bodies other than albumin.   As has been recently shown, non-albuminous urine of persons taking quinine will give a precipitation with this test; so also will the partially transformed albumins known as peptones.

ALBUMIN TEST-PAPERS.   Dr. George Oliver, of London, has advised and used with much success the reagents for albumin, in the form of slips of filter paper which have been soaked in the solutions and then dried. They are used by dropping them into the urine to be tested.   As the efficacy of the tests depends on the urine being acid, a citric acid paper is also provided, which may in a similar manner be first dropped into the urine.   The papers should be placed at the bottom of the tube, and it then allowed to stand for a minute or so without shaking.   If albumin be present a white cloud will form around the paper.   The papers may also be used by placing them in a circle so as to fit within the test-tube, then near the bottom.   The liquid to be tested is then poured in, to above the level of the paper.   If albumin be present the liquid below the paper becomes cloudy.

Sugar.   Traces of sugar are sometimes found in the urine of apparently healthy persons, but its presence in appreciable quantities is to be considered an indication of disease.   The form that occurs in urine is technically known as *dextrose* or *dextro-glucose;* it is different in many properties from common table sugar, but identical with the ordinary glucose or starch sugar now so much used as an adulterant.   The tests for the presence of dextrose are mostly dependent upon its reducing action upon metallic salts.

TROMMER'S TEST.   When an alkaline solution of sugar is boiled with a solution of copper a salmon-colored precipitate of cuprous oxide, Cu_2O, is formed.   To apply the test, add to about 1 fluid drachm (8 c.c.) of filtered urine enough copper sulphate solution to give a faint greenish-blue tinge, and then, at least twenty drops of a strong solution of caustic potassa or soda.   The mixture must then be heated to boiling, when, if sugar be present, the cuprous oxide will be thrown down, often as a greenish-yellow precipitate at first, but which becomes, on further boiling, a bright salmon color.   If no sugar is present the precipitate will be bluish-green, and upon further boiling, will turn black.   When much sugar is present the liquid, before boiling, will appear clear blue, and the deposition of the cuprous oxide will occur in the cold.

MOORE'S TEST.   Moore's test consists in adding caustic alkali to the filtered urine and then boiling.   If sugar be present the urine will become considerably darker, but usually remains clear.   The depth of the color

will depend upon the duration of boiling, the quantity of sugar and the strength of the alkali.   If to the urine so colored a few drops of nitric acid are added, the color is diminished and an odor of burnt molasses is produced.

FERMENTATION TEST.   The conversion of sugar into alcohol is one of the most direct evidences of its presence.   The occurrence of fermentation is shown by escape of gas bubbles.

BOETTGER'S TEST.   Add to a fluid drachm (4 c.c.) of filtered urine about half its volume of solution of caustic potassa or soda, and then a pinch of bismuth subnitrate.   Shake the mixture and boil for a minute or so.   Presence of sugar will be indicated by a *black* precipitate of metallic bismuth.   If sugar is not present the precipitate will be white, or at most, somewhat gray.   The action does not take place unless considerable free alkali is added.   This test is very delicate and tolerably free from fallacy.   Dark-colored urines of high gravity generally produce a gray precipitate, which might be considered an indication of the presence of small amounts of sugar.   The precipitate is not so heavy as metallic bismuth, and does not settle so rapidly nor so completely to the bottom of the tube.   Silver chloride is often present as an impurity in commercial bismuth subnitrate, and the organic matter of the urine will cause a brownish precipitation of metallic silver, which cannot be distinguished from metallic bismuth.   For proper use, therefore, it is better to purify the bismuth nitrate by dissolving the commercial article in nitric acid, adding a few drops of hydrochloric acid, filtering and pouring the filtrate into a large volume of cold water.   The precipitate collected, washed and dried, is in excellent condition for use.   As a convenient method of applying Boettger's test I have devised the following mixture :—

Bismuth subnitrate,	½ drachm	(2 grams)
Quicklime,	1 . "	(4 grams)
Sodium carbonate (dry) 1	"	(4 grams)

These substances are powdered and thoroughly mixed and kept in a *closely stopped* bottle.   A small quantity added to the urine and boiled will give the test very well.   I have kept this mixture in good condition for several months.

SOLDAINI'S TEST.   Copper carbonate, obtained by precipitating copper sulphate with sodium carbonate, filtering and washing the precipitate, is dissolved in about 25 times its weight of acid sodium carbonate (baking soda), and the blue solution allowed to settle until clear.   When this is boiled with urine containing sugar, cuprous oxide is thrown down, in its usual form.   Milk sugar also causes the same action, but cane sugar

does not. This is the best form of the copper test with which I have experimented. It is more trustworthy than Fehling's solution. Instead of dissolving the materials they may be conveniently used in the form of powder, in the same manner as has been suggested in connection with the bismuth test.

OLIVER'S TEST—INDIGO CARMINE; SODIUM SULPHINDIGOTATE. We owe the introduction of this solution to Dr. George Oliver, of London. It is made by dissolving indigo in strong sulphuric acid and neutralizing its solution exactly with sodium hydrate. This solution, which has an intense blue color, is then mixed with sodium carbonate; the indigo salt is thus precipitated in a fine state of division, but may be dissolved by the aid of heat, giving a greenish-blue liquid. When this liquid is heated with glucose the color becomes distinctly green, then red, then yellow.

The solution of indigo-carmine and sodium carbonate does not keep well. To obviate this difficulty, Dr. Oliver has used papers prepared by soaking strips of filter paper in the solution, and drying carefully. These papers are used by placing one of them in about a drachm of water, which is then heated to boiling for a few seconds. The solution should become a deep, clear blue. (Water containing calcium salts produces a turbid solution, which may be prevented by dropping in a paper which has been impregnated with sodium carbonate.) After the solution has been boiled, one drop of the suspected urine is put in and the liquid boiled again for a few seconds, then raised above the flame and kept hot, without boiling, for one minute. If glucose is not present in abnormal amount the color will be unchanged, but if it is, the blue will turn to violet; then purple, red, yellow and straw-yellow will successively appear. If the solution is allowed to remain exposed to the air, the colors will reappear in the reverse order. (See Appendix.)

QUANTITATIVE ANALYSIS.

Quantitative determination of a few of the normal and abnormal ingredients of urine is occasionally necessary, for purposes of diagnosis or prognosis, or for determining the efficacy of methods of treatment. The substances so determined are uric acid and urea, among the normal ingredients, albumin and sugar among the abnormal.

Uric Acid. The method most convenient for estimating uric acid is not quite accurate, but suffices for clinical purposes. One hundred c.c. (3 fluid ounces) of the urine is mixed with ten c.c. (2½ fluid drachms) strong

hydrochloric acid, and set aside for twenty-four hours, in a cool place. Fine crystals of uric acid separate, which are to be collected on a filter which has been dried at 212° F. and weighed, thoroughly washed with dilute hydrochloric acid, dried, and the weight of the filter and acid less that of the filter itself, is the weight of the uric acid. As the acid is slightly soluble in water there is some loss, amounting to about $\frac{1}{10}$ grain for every 200 c.c. of water.

Phosphoric Acid. The best process of estimating this body would be to acidify 33 c.c. (1 fluid ounce) of the urine with nitric acid and add solution of ammonium molybdate. After standing for an hour or so in a warm place the precipitate—ammonium phospho-molybdate—is collected on a filter, washed with water acidulated with nitric acid, then dissolved in dilute ammonia. To this solution is added a mixture of magnesium sulphate and ammonium chloride, and the resulting precipitate is collected on a filter, washed with very dilute ammonia water, dried, burned, and weighed. The weight multiplied by 0.64 will give the amount of phosphoric anhydride, P_2O_5.

A volumetric process with uranium solution is used, but it is difficult to obtain reliable results with it.

Several approximate methods of estimating phosphates have been devised. These are sufficiently accurate for most clinical purposes.

For the so-called earthy phosphates, Hoffmann and Ultzmann recommend that a test-tube, about six inches in length and three-quarters of an inch wide, should be filled one-third full with the clear urine, and a few drops of ammonia or caustic soda be added, and the mixture heated slightly. The phosphates will separate in flakes, and in fifteen minutes will have subsided, if the tube is left at rest. If the layer of sediment is about one-third an inch high the amount is normal; any marked departure from this can be easily noted.

The alkaline phosphates may be estimated by adding to the urine about one-third its volume of a mixture made with about equal parts of magnesium sulphate, ammonium chloride and ammonia, dissolved in about eight times the quantity of water. A normal quantity of alkaline phosphates will give with this mixture a uniformly *milky* appearance.

Urea. Several methods of estimation are in use, but the one known as the hypochlorate process is most convenient for clinical use. It depends on the fact that a solution of a hypochlorite will decompose urea, and liberate its nitrogen in the free state. This nitrogen being collected and measured will, by calculation, give the amount of urea present. Dr. Squibb, of

Brooklyn, New York, has lately presented a description of this method as modified by him, and it is here given in full.*

DESCRIPTION OF APPARATUS AND MODE OF USING IT.

The apparatus consists of two four-ounce wide-mouth vials, two good corks which fit the mouths of the vials accurately, two short, small, glass tubes bent at right angles, and one straight tube, all three rounded in the lamp, at the ends, so that rubber tubing slips over them easily and tightly; two pieces of pure rubber tubing of about 3 m.m. or ⅛ inch bore; a small glass or wooden plug of proper size to stopper the rubber tubing; a narrow glass jar or homœopathic vial which will pass through the neck of one of the vials, and of about 5 c.c., or 80 minims capacity; a pair of small forceps with which to pass the jar into the vial; and lastly, a graduated pipette of 5 c.c., or 80 minims capacity. The other essentials, which every physician and pharmacist has always at hand, are a block, or two or three books on which to lay one of the bottles; a common two-ounce vial and a block or book to set it on, and a two-ounce graduated measure. For rough work a common minim measure may supply the place of the more accurate graduated pipette.
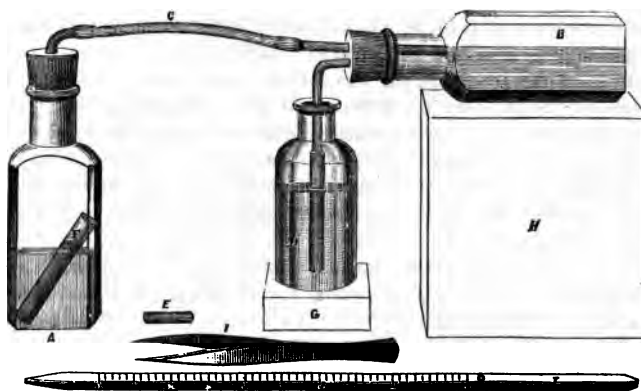
The illustration represents the apparatus at the end of a determination, while standing to allow of adjustment of temperatures before measuring the result. A and B are the two four-ounce wide-mouth vials, one of which, at least, should be square, in order to avoid rolling when laid on its side.

*I condense the description of this method from an account of it in the *Pharmaceutical Record* for March, 1884, and I am indebted to Prof. Bedford, the editor of that journal, for his kindness in allowing the use of the cut of the apparatus required. H. L

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Those shown in the cut are the ordinary bottles in which pills are put up, and they answer very well, and are easily accessible everywhere. Although ordinary corks are suitable, rubber corks are better and more durable.   If ordinary corks be used, they should be soaked in water before using, and be put in wet.   If rubber corks be used, they should be put in dry, the mouth of the vial being also dry; otherwise they are difficult to keep in place. One cork has two perforations and the other has one, and these are occupied by short glass tubes, as shown.   C is a piece of rubber tubing about 20 c.m. or 8 inches long, which connects the two vials, for the passage of gas. D is the receiving vial for the displaced water, and a piece of rubber tubing passes down into this to conduct the water into it, and long enough to be below the surface of the water at the end of the operation, even though the water be small in quantity.   E is the little plug used to stop the end of this short rubber tube before the operation is commenced.   F is the urine jar which holds its charge from contact with the decomposing liquid while the apparatus is being charged and adjusted.   G is the block about 25 m.m. or 1 inch thick, to support the receiving vial in place during the operation. H is the block or books for supporting the vial in which the gas displaces the water. I is the forceps for lowering the urine jar into the vial where the decomposition is to be effected, and J is the graduated pipette for measuring the urine and the displaced water.

In using the apparatus, put into vial A 40 c.c. or 1⅓ fluid ounces of officinal U. S. P. Solution of Chlorinated Soda.   Measure accurately into the urine jar F, 4 c.c. or 64 minims of the urine, and by means of the forceps I, or some other device, as a loop of thread, place the charged urine jar in the solution of vial A in the position shown in the cut, and put the stopper securely in place, having the long rubber tube slipped on to the short glass tube.

Fill vial B nearly full of water of the temperature of the room.   Put the short rubber tube on the bent glass tube of the stopper of B, and then put the stopper firmly in place.

Then holding vial B, thus stoppered, in the right hand, with the forefinger over the end of the straight glass tube, incline the vial toward the bent glass tube until that and the short rubber tube on it fill with water. When filled, stop the flow by closing the end of the straight tube with the finger, and with the left hand put the little stopper E into the end of the short rubber tube while this tube is full of water.

Then lay the vial B on its side on the support, as shown, and slip the free end of the long rubber tube C on to the straight glass tube of the *stopper of B, thus connecting A and B.*

Put a piece of waste paper under the end of the short rubber tube, and then take out the little stopper E. A few drops of water will usually escape, but if the apparatus be tight, and if the temperature of the apparatus and the room be the same, no more water will run out, nor will any air enter.

A common two-ounce vial D, or any other similar vessel, is to be used for receiving the displaced water. Rinse it out and drain it for a moment, so as to leave the inner surfaces wet, as they will be left when it is emptied for measurement of the water, and then put it in its place under the short rubber tube, as shown, and the apparatus is then ready for the process.

Incline the vial A until the urine and solution mix, and agitate the mixture gently sidewise until the effervescence ceases, being sure that a full interchange of liquids between the jar and vial is effected. When the effervescence is at an end, and no further movement of gas into B occurs upon pretty vigorous agitation, let the apparatus stand a quarter or half hour, to regain the room temperature. The time required to equalize the temperature may be shortened to about ten minutes by immersing vial A in a bath of water at the room temperature. During this cooling a little water will pass back from D into B, and from B into A, and when this movement is at an end, the water in D is to be carefully measured, with the pipette J, into another vessel, from which the measurement can be verified if necessary.

In measuring this displaced water from D, 5 c.c. at a time, care must be taken in the counting. At the end there will almost always be some fraction of 5 c.c. to measure, and this is best done in the following way :—

Reverse the pipette, and by suction at the point or small end draw in water from any source of supply, to half fill the pipette. Then, with the finger on the small end, let the water run out until the o mark of the graduation is exactly reached. Then the upper or blank end of the pipette, from the o mark upward, will be exactly filled. Allow this water to run into that which remains in D, and be thus added to it. Then draw the whole into the pipette, stop the upper end quickly with the finger so as to keep it all in, and then reverse the pipette with the upper end stopped, and read off the quantity by the graduations, the water which occupies the ungraduated part being that which has been added, and therefore not to be counted.

Each c.c. of this displaced water is equal to a c.c. of the nitrogen which displaced it; and each c.c. of nitrogen represents .0027 gram of urea. Therefore the number of c.c. of water represents the number of times .0027 gram of urea contained in 4 c.c. of the urine. But it is more simple and easy to obtain the percentage of 1 c.c. of urine, and, therefore,

the number of c.c. of displaced water is divided by 4. Then this number being multiplied by .0027 gives the percentage of urea in the urine.

For example, suppose the displaced water from 4 c.c. of urine be 36 c.c. This divided by 4 gives 9 c.c. for each 1 c.c. of urine. Then 9 times .0027 is .0243. Then, as this quantity of urea comes from 1.000 c.c. or 1.000 gram, it must be multiplied by 100, in order to give percentage, and this is the same thing as moving the decimal point two places to the right, or between the 2 and the 4. Hence the urine contained 2.43 p.c. of urea.

If minims and grains be used instead of cubic centimetres and grams, the calculation is precisely the same, only less simple. The 64 minims of the same urine would give 584.27 minims of displaced water.

Each minim of displaced water represents .0027 grains of urea. Therefore the 584.27 multiplied by .0027 grain gives 1.577529 as the total urea from 64 minims of urine. Then the 1.5775 divided by the 64 minims gives .0246 + grain of urea for each minim, and this multiplied by 100 gives 2.46 p.c. urea for the urine.

To apply these figures to the total urine of the 24 hours, the whole is measured in c c. or in fluid ounces. If in fluid ounces, it is better to reduce this to minims by multiplying by 480, or the number of minims in the fluid ounce.

Suppose the urine for the 24 hours be 1200 c.c. or 40 fluid ounces. If 1200 c.c., then 2.43 p.c. of this quantity is (1200 × 2.43 = 2916.00 ÷ 100 =) 29.16 grams as the total excretion of urea for the 24 hours. If 40 fluid ounces or (40 × 480 =) 19,200 minims, then 2.46 p.c. of this quantity is (19,200 × 2.46 = 47,232.00 ÷ 100 =) 472.32 grains as the total excretion for the 24 hours.

It may be as well to note, in conclusion, that any kind of solution of chlorinated soda will not answer for this purpose, any more than for medicinal uses, as the markets are supplied with some which contains very little hypochlorite of soda; but any solution that is made in moderately close accordance with the U. S. P., either of 1870 or 1880, will answer well, no matter how old it is, if it has not been too long, or too much, exposed to the air, and a pound of such a solution, costing not over 30 or 40 cents, makes ten or eleven determinations.

An approximate table may be easily given which will be found fairly accurate to the second decimal place, and figures intermediate to those given may easily be interpolated. The basis of the table is 1 c.c. of nitrogen equivalent to .0027 gram of urea, and the first and second columns apply to the measurement whether of the gas or of the water displaced by the gas. The standard quantity of the urine which yields the *results* given is 4 c.c. or 64 minims.

UREA TABLE.

One cubic centimetre of nitrogen equal to .0027 gram of urea, or one minim volume of nitrogen equal to .0027 grain of urea.
Four c.c. or 64 minims of urine give the columns of Results of Process.

RESULTS OF PROCESS.		Percentage of urea indicated.	Urea in the 24 hours for each 473 c. or one pint of urine excreted.	
In c.c.	In minims.		In grams.	In grains.
15	243	1.01	4.78	73.8
16	260	1.08	5.11	78.9
17	276	1.15	5.44	84.0
18	292	1.22	5.77	89.0
19	308	1.28	6.05	93.4
20	325	1.35	6.39	98.6
21	341	1.42	6.72	103.7
22	357	1.49	7.05	108.8
23	373	1.55	7.33	113.1
24	390	1.62	7.66	118.2
25	406	1.69	7.99	123.3
26	422	1.76	8.32	128.4
27	438	1.82	8.61	132.9
28	454	1.89	8.94	138.0
29	471	1.96	9.27	143.1
30	487	2.03	9.60	148.1
31	503	2.09	9.89	152.6
32	519	2.16	10.22	157.7
33	536	2.23	10.55	162.8
34	552	2.30	10.88	167.9
35	568	2.36	11.16	172.2
36	584	2.43	11.49	177.3
37	600	2.50	11.83	182.6
38	617	2.57	12.16	187.7
39	633	2.63	12.44	191.8
40	649	2.70	12.77	197.1
41	665	2.77	13.10	202.2
42	682	2.84	13.43	207.3
43	698	2.90	13.72	211.7
44	714	2.97	14.05	216.8
45	730	3.04	14.38	221.9
46	747	3.11	14.71	227.0
47	763	3.17	14.99	231.3
48	779	3.24	15.33	236.6
49	795	3.31	15.66	241.7
50	811	3.38	15.99	246.8
51	828	3.44	16.27	251.1
52	844	3.51	16.60	256.2
53	860	3.58	16.93	261.3
54	876	3.65	17.26	266.4
55	893	3.71	17.55	270.9
56	909	3.78	17.88	275.9
57	925	3.85	18.21	281.0
58	941	3.92	18.54	286.1
59	958	3.98	18.83	290.6
60	974	4.05	19.16	295.7

The use of this table is simple enough. The observer finds at the end of the twenty-four hours that, starting with the bladder empty, he has 1200 c.c. or 40 fluid ounces of urine. Of this he or the nurse assays 4 c.c. or 64 minims for urea, and obtains a result of either 36 c.c. of gas or displaced water, or of the equivalent of this in the other way of measuring, namely, 584 minims of displaced water. Having either the 36 c.c. or the 584 minims, he refers to the table under the double column of " Results of Process," and he follows down the column whose denomination he has until he reaches the number 36 or 584. He then follows this line horizontally across the page, and finds, first, that the urine contains 2.43 per cent. of urea; and next that this is equivalent to 11.49 grams in 473 c.c. of the urine; and next that it is equal to 177.3 grains of urea in one pint of 16 fluid ounces of the urine.

Now, if 473 c.c. of the urine contains 10.49 grams of urea, the whole 1200 c.c. will contain (As 473 : 11.49 :: 1200 :) 29.15 grams as about the amount excreted in twenty-four hours.

Then if 1 pint of the urine contains 177.3 grains of urea, the whole 40 fluid ounces, which being exactly 2½ pints, will contain just 2½ times that much, namely: (177.3 $\times$ 2.5 =) 443.3.

For quantitative determination of sugar and albumen, see Appendix.

Urinary sediments. The sediments which form in urine may be either organized or unorganized. All the forms require the microscope for their satisfactory identification. The organized sediments are principally tube-casts, blood or other corpuscles, epithelial cells, and spermatozoids. Many matters entirely foreign to the urine may find their way into it, either by design or accident. I have known a deposit of collodion and iodoform to be mistaken for a urinary sediment, and attempts made to induce physicians to believe that a piece of brick was a urinary calculus. Those who use the microscope for urinary analysis should familiarize themselves with the appearance of common objects, such as hair of various kinds, cotton and other fibres, fragments of wood, milk globules, etc.

The unorganized sediments are principally uric acid, urates, phosphates and oxalates. Uric acid is generally in lozenge- or boat-shaped crystals. Urates are in indistinctly crystalline; phosphates are generally in distinct prismatic crystals; oxalates in small, regular octahedra.

Dr. Formad has recently given a summary of the characteristics of the urinary sediments:—

A sediment has no significance unless formed within twenty hours after the urine has been passed.

Every white crystal is a phosphate or oxalate; the distinction may be

made by the microscope. Every yellow crystal is uric acid if the urine be acid, or a urate if it be alkaline.

URINARY CALCULI.

The common forms of urinary calculi are composed of either uric acid, earthy phosphates, or calcium oxalates. Potassium sodium, or calcium urate, may also be found, and two bodies—xanthine and cystine—are found quite rarely. The common calculi are generally mixtures of several of the above mentioned bodies. Calcium oxalate and uric acid often form the nuclei, around which other matters deposit. The distinction of the different forms is based principally on the action of heat on them.

1. A portion of the calculus is heated to redness on a piece of platinum foil. *a.* No residue is left. See 2. *b.* A fixed residue is left. See 3.

2. Apply the murexide test, page 98. If this gives a result, the calculus is either uric acid or ammonium urate. If no result occurs, the substance is either xanthine or cystine. See 5.

3. Add a drop of hydrochloric acid to the residue, when cold. *a.* It effervesces. The original body was either a urate or oxalate. See 4. *b.* It does not effervesce. The calculus is a phosphate. The result may be confirmed by dissolving a portion of the calculus in hydrochloric acid, and adding ammonium molybdate; a yellow precipitate will be formed.

4. Apply the murexide test to a portion of the original body. If it responds, the body is a urate, if not, an oxalate.

5. The solution of the original body in nitric acid turns yellow, on evaporation, and leaves a residue insoluble in potassium carbonate: xanthine. The solution in nitric acid turns dark brown and leaves a residue soluble in ammonia: cystine.

SANITARY CHEMISTRY.

Sanitary chemistry includes the examination of food, water and air, and the determination, as far as possible, of the purity of these and their fitness for use. The impurities may be either substances which are intentionally added, accidentally introduced, or be formed in the articles by decomposition or other chemical changes. Articles of food and drink are now largely adulterated, but fortunately very few of these adulterations are injurious. Analyses of food, water and air are very difficult when fully performed, but for many substances easy methods are known which suffice to detect flagrant adulterations or serious contamination. It will be sufficient to enumerate a few articles and indicate the tests.

DRINKING WATER.

Perfectly pure water can be obtained by careful distillation, collecting those portions which come over during the middle of the operation. The purest natural forms are rain water collected in open country, and spring water issuing from the harder rocks.

The substances present in natural water are of two kinds, mineral and organic. The mineral substances are generally sulphates, chlorides and carbonates of calcium, magnesium and sodium. The organic matters are indefinite in character and as yet not well understood. The exact analysis of water is a somewhat difficult problem, but for sanitary purposes very good results can be obtained in a short time by processes now known. It is at present not possible to say how the various mineral substances enumerated above affect the health, but the organic matters undoubtedly produce very marked action, and their determination is the most important. The examination of water with a view to determine its suitability for drinking purposes may be limited to the following points.

Chlorine. This always exists in combination as chloride. It is conveniently determined by using a solution of silver nitrate of known strength. Chlorides in themselves have no special effect, injurious or beneficial, but as sewage, urine and waste material generally contain a decided amount of common salt (NaCl), the presence of any marked amount of chlorine is considered an indication of contamination by these liquids, unless some other source should be apparent. Thus, near the sea a high percentage of chlorine would have little significance. Low proportion of chlorine does

not always indicate pure water, because vegetable contamination does not add much chlorine.

A rough idea of the quantity of chlorine may be obtained by observing the amount of turbidity produced by adding a few drops silver nitrate and of nitric acid to about an ounce of the water. A proportion of chlorine equal to one grain to the gallon gives a haze; four grains gives a marked precipitate.

Nitric acid must always be added to water when testing for chlorine, as carbonates will otherwise be precipitated.

A quantity of chlorine less than one grain per gallon is not regarded as indicative of sewage under any circumstances.

Hardness. This is due to calcium and magnesium salts present. They prevent the water forming a lather with soap, because they precipitate the soap in an insoluble form. Waters containing but little of these salts are said to be soft. The degree of hardness is determined from the number of measures of a standard soap solution which have to be added before a permanent lather is formed. Hardness may be either temporary or permanent. Temporary hardness is due to calcium or magnesium carbonates, which are held in solution by free carbonic acid, and are therefore precipitated when the water is thoroughly boiled. Permanent hardness is due to calcium or magnesium sulphate or chloride, and these are not precipitated when the water is boiled. Much doubt still exists as to the comparative wholesomeness of hard and soft water. When the hardness is very great the water is probably not suitable for continued use. The exact determination of hardness, especially of the difference between temporary and permanent hardness, is difficult, but any marked degree of temporary hardness is usually indicated by a precipitate on boiling the water for a few minutes.

Oxygen required for organic matter. The organic substances in water can be burned up and destroyed by oxidizing agents, and the amount of oxygen required for this purpose can be used to indicate the quantity of organic matter present. These processes, however, are not very exact in practice, and hence have only indirect value. The substance commonly used as the oxidizing agent is potassium permanganate, the distinct color of which enables us to see when it has been added in excess. The process originally used by Forchammer has been improved by Tidy, who has given directions by which the best results are obtained. The following is a rough form of Tidy's method, suitable for those who are not experts in volumetric analysis.

Solutions are prepared as follows :—

Standard permanganate, made by dissolving 0.395 gram potassium permanganate in 1 litre of water free from organic matter.

Dilute sulphuric acid, made by diluting a good quality of sulphuric acid with twice its volume of water, and adding permanganate until a faint tint is produced, which remains for a few seconds.

From three to six glass bottles or flasks holding about 250 c.c. (8 f ℥) are washed clean and filled with equal quantities of the water. Ten c.c. of the sulphuric acid is then put into each, and amounts of the standard permanganate are put in, varying from one c.c. to six c.c. or more, according to the number of bottles. Each bottle is then closed by laying a piece of clean tin foil over the mouth, and set aside in a dark place, preferably at a temperature of about 75° or 80° F., for 3 or 4 hours. On examining the series of bottles, it will generally be found that some have been completely decolorized and others not, and if the bottles have been properly marked it is easy to find the number of c.c. which is just sufficient to tint the water, and therefore contain a little more oxygen than is required for the organic matter. Each c.c. of standard permanganate corresponds to .0001 gm. O. The amount of oxygen absorbed by a water ought not to exceed .03 parts per 100,000.

Silver nitrate test for organic matter. If a solution of silver nitrate made alkaline by ammonia be added to water the precipitation of chloride will be prevented and the water will in almost all cases remain clear. If the liquid be now exposed to sunlight a degree of discoloration will be produced, depending in part on the amount of organic matter present. I have usually performed this test by adding about ten drops of a strong solution of silver nitrate, made alkaline by ammonia, to four ounces of the water, and exposing the liquid to the sunlight for two hours. Good water will show but little tint at the end of this time.

Sulphates. These are detected by adding to a portion of the water a few drops of nitric acid and then barium nitrate. A white precipitate will indicate the sulphates. The sulphates present in water are generally those of calcium and sodium; free sulphuric is rarely found; it can be detected by its action on litmus. The free acid is objectionable, but nothing is known to indicate that the other sulphates are injurious.

Calcium compounds. Calcium carbonate and calcium sulphate are frequently found in water. They may be detected by the formation of a white precipitate on the addition of ammonium hydroxide and ammonium

oxalate. Any considerable amount of calcium carbonate will usually be indicated by a precipitate on boiling the water.

Metallic impurities. Iron, lead, copper and arsenic are occasionally found in water, and with exception of the first named may be regarded as injurious, even when in very small quantities. Copper, however, appears to be without direct effect when in very small quantities. The best test for these metallic impurities is hydrogen sulphide, which produces precipitates. Any water which gives a colored precipitate or even a brown tint with this test should be rejected. (See Appendix.)

ARTICLES OF FOOD.

Milk. The composition of milk is given elsewhere. These proportions do not vary much except when the milk is tampered with, either by adding water or abstracting cream. The specific gravity of pure milk is about 1.030 but this cannot well be used as a standard of purity, as, owing to butter being lighter than water, very rich milks are below the standard as well as watered milks. It is true that such rich milk will show its richness by giving more cream; but such a test will detect flagrant adulteration only. Dr. Letheby has given a table of the ratio between specific gravity and cream-yielding power of pure and watered milk :—

	Sp. Gr.	*Per Cent. of Cream.*	*Sp. Gr. when skimmed.*
Pure milk...........................	1.030	12	1.032
10 per cent. water added...........	1.027	10.5	1.029
20 " " "	1.024	8.5	1.026
30 " " "	1.021	6.0	1.023

Genuine milk is of a full white color and opaque. The only accurate method of analysis is by evaporating a known weight of a sample, extracting the fat by means of ether and weighing it.

Under the microscope milk should exhibit nothing but round oil globules which do not run together and a few epithelial cells.

Butter. Genuine butter is merely the fat of milk, the oil globules having been made to coalesce by churning. It is largely adulterated with water and salt. The proportion of these may be approximately determined by melting some of the sample in a test-tube, by which the salt and water will go to the bottom. Good butter is nearly all soluble in ether. More than fifteen per cent. of water or five per cent. of salt can be regarded as adulteration. Substitutes for butter are now largely sold under the names oleo-margarine, butterine and suene. These are made

from animal fats, tallow or lard, or from vegetable oils, and are often mixed with milk or true butter, to more effectually conceal the adulteration. The detection of the substitution is often difficult, but fortunately they have very little sanitary importance, as they are, if properly and cleanly made, as nutritious as butter itself.

Pure butter, if melted and filtered while warm, will retain its color and odor, but most butter substitutes will become paler and lose odor.

Flour. Alum is occasionally mixed with flour, in order to improve the appearance of the bread made from it. It is also put in, in combination with baking soda, to give a self-raising quality to the flour. There is no evidence that it is injurious, and it must be remembered that when associated with baking soda, alum is converted in alumina, as soon as the flour is mixed with water.

Coffee is not much subject to adulteration, because it is generally sold unground. Ground coffee is liable to contain chicory, burnt peas, beans, and similar substances. These may sometimes be detected by the microscope or determination of ash, etc., but the processes are difficult. Pure ground coffee when thrown into cold water communicates but little color; if chicory be present the water will be colored.

The substances sold in boxes as coffee-essences are usually gross frauds, containing no coffee at all. Preparations known as liquid coffee are now sold. These are generally *bona fide*, being water-extracts of good coffee mixed with some preservative.

APPENDIX.

A. Winter Blyth has recently described the following delicate test for lead in water :—

"A solution of cochineal is prepared by boiling the ordinary commercial cochineal in water, filtering, and then adding sufficient strong alcohol to insure its preservation from mold. A few drops of this solution, added to a colorless neutral or alkaline solution containing dissolved lead, strikes a deep mauve blue to a red with a faint blue tinge, according to the amount of lead present. The test will distinctly indicate a tenth of a grain of lead per gallon in ordinary drinking water, and by comparison with a solution free from lead, much smaller quantities are indicated.

"In searching for traces of lead in water, it is convenient to take two porcelain dishes; into one place 100 c.c. of the water to be examined, and into the other a solution of carbonate of lime in carbonic-acid water, known to be lead free, and approximately of the same hardness as the water to be examined; then add to each an equal bulk of the coloring matter in quantity sufficient to distinctly tinge the water; the colors may now be compared; the slightest blue tint will be either due to lead or copper, for copper in very dilute solutions gives a similar tint, but in solutions of 1 to 1000, or stronger, the hue is so different as to differentiate the two metals.

Trichloracetic Acid, $HC_2Cl_3O_2$, as a test for albumin. This acid is a white, crystalline, deliquescent solid, which dissolves easily in water and coagulates albumin. Its use as a test is of recent date. It is employed in the same manner as meta-phosphoric acid, but, as it dissolves decidedly more easily, the coagulation is formed rather more rapidly. I have not found it more delicate than the other tests, but have not yet made extended experiments. It is very convenient for use; quite as convenient, even, as the urinary test papers. It is a distinct acid, and will, therefore, probably be subject to the same fallacies that such tests as picric or nitric acid are.

Quantitative estimation of albumin is generally only approximately determined by judging from the depth of the white ring formed in the nitric acid test. According to Hoffmann, and Ultzmann, if this ring has a depth of $\frac{1}{12}$ to $\frac{1}{4}$ inch, is pale white, and is seen only when placed against a dark background, the quantity of albumin is less than one-half

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per cent.   If the ring appears snow-white, opaque, and easily recognizable,
then there is about ½ per cent. of albumin.   If the precipitate is in flakes,
and heavy enough to fall to the bottom and make the liquid creamy, the
quantity is large—one to two per cent.

Picric acid as a test for sugar.   When a solution of picric acid,
made alkaline with caustic soda, is boiled with glucose, the yellow color
of the solution is turned to a fine brown-red in a few seconds.   This test
may be very conveniently used for both qualitative and quantitative
determination of sugar, as has been shown by Dr. George Johnson, of
London.

A standard solution of sugar, for comparison, is first made by dissolving
one grain of sugar in an ounce of distilled or rain water.   One drachm
of this is mixed with ten minims of a saturated solution of picric acid in
water, and excess of caustic soda added.   The solution is boiled for about
a minute, and the liquid then diluted to make four drachms.   As this is
four times the bulk of the original sugar solution taken, the color so
obtained corresponds to a proportion of one-quarter grain to the ounce.
Dr. Johnson finds that this solution does not keep well, and uses, instead,
a solution of ferric acetate, to which is added acetic acid and excess of
ferric chloride.   This liquid is diluted with water until the depth of color
corresponds to that of the standard liquid.   The standard liquid is kept
in the dark, when not in use, for comparison.   The quantitative examina-
tion of a sample of urine is performed as follows: A rough estimation
as to whether a small or large quantity of sugar is present is made from
the specific gravity, and to a fluid drachm add ten minims of the saturated
picric acid solution for every grain of sugar per ounce of the urine, and
then excess of caustic soda.   That is, if it should be judged that the urine
contains about four grains of sugar per ounce, to a fluid drachm of the
sample should be added forty minims of the picric acid.   The liquid is
then boiled for about a minute, cooled, and made up to four drachms in
volume; then a definite portion of this is diluted, cautiously, until it
equals in tint the comparison tube of ferric acetate.   From the degree of
dilution the amount of sugar is determined.   For instance, if the urine
contained one grain to the ounce it would, when diluted to four drachms,
be equal to the standard tube and require no further dilution, as the
standard corresponds to the color given by that amount of sugar.   If the
liquid contains two grains to the ounce the four drachms would have to
be diluted with an equal bulk of water before equalling the standard tube,
thus showing that the liquid was twice as strong as the standard.   Dis-
tilled or rain water should be used for diluting.   The liquid to be

compared should be in tubes of equal size and quality. Albumin does not appear to interfere with the test. In cases in which the proportion of sugar is entirely unknown, several experiments will have to be made with different proportions of picric acid solution, until the proportion is found beyond which no further deepening of color occurs when more acid is added.

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